PROCEEDINGS

OF THE

NATIONAL INSTITUTE OF SCIENCES OF INDIA

VOL. III

1937

CONTENTS

No. 1—April, 1937.

No. 2—April, 1937.

Second Annual General Meeting.

The Second Annual General Meeting of the National Institute of Sciences of India was held at 3 P.M. on Tuesday the 5th January, 1937 in the Address Hall of the Osmania University, Hyderabad, Deccan.

The following Fellows were present :—

Brigadier H. J. Couchman, *President* (in the chair).
Prof. B. Sahni, Vice-President.
Dr. S. L. Hora, *Honorary Treasurer.*
Prof. M. N. Saha, *Foreign Secretary.*
Prof. S. P. Agharkar, *Honorary Secretary.*

Mr. T. P. Bhaskara Shastri.	Prof. M. Qureshi.
Prof. S. N. Bose.	Dr. B. Sundara Raj.
Prof. W. Burridge.	Dr. K. R. Ramanathan.
Mr. H. G. Champion.	Dr. L. A. Ramdas.
Prof. S. Datta.	Rao Bahadur G. N. Rangaswami Ayyangar.
Khan Bahadur M. Afzal Husain.	Mr. P. R. Ray.
Prof. K. S. Krishnan.	Prof. V. Subrahmanyan.
Prof. J. N. Mukherjee.	Rao Bahadur T. S. Tirumurti.
Prof. K. G. Naik.	Rao Bahadur T. S. Venkataraman.
Prof. P. Neogi.	Rao Bahadur B. Viswa Nath.
Dr. H. S. Pruthi.	Mr. D. N. Wadia.

Mr. W. D. West.

The meeting was also attended by 61 visitors.

1. The minutes of the Fourth Ordinary General Meeting were read and confirmed.

2. The President appointed Dr. S. Datta and Dr. B. Sundara Raj to act as scrutineers of the ballot papers received for the election of officers and other members of the Council for the year 1937.

3. The following Ordinary Fellow was admitted as a Fellow as per Rule 13.

Prof. P. Neogi.

4. Prof. K. G. Naik, Rao Bahadur T. S. Venkataraman and Rao Bahadur B. Viswa Nath signed the duplicate obligation form as per Rule 13.

5. The Annual Report prepared by the Council was adopted (see pp. 3–20).

6. The President delivered his annual address, the subject being ' Progress of Geodesy in India ' (see pp. 21–28).

7. The following were declared to have been elected officers and other members of the Council for the year 1937.

President: Prof. M. N. Saha.
Vice-Presidents: Prof. S. S. Bhatnagar and Brevet-Col. R. N. Chopra.
Treasurer: Dr. S. L. Hora.

Foreign Secretary: Prof. B. Sahni.
Secretaries: Prof. S. P. Agharkar and Dr. A. M. Heron.

Members of Council: Mr. T. P. Bhaskara Shastri, Dr. G. S. Bose, Sir Bryce C. Burt, Prof. J. C. Ghosh, Dr. F. H. Gravely, Khan Bahadur M. Afzal Husain, Prof. K. S. Krishnan, Dr. R. B. Lal, Prof. S. K. Mitra, Prof. J. N. Mukherjee, Dr. C. W. B. Normand, Dr. Baini Prashad, Prof. N. R. Sen, Lt.-Col. S. S. Sokhey, Col. J. Taylor, Mr. C. G. Trevor, Prof. B. Venkatesachar, Mr. F. Ware.

8. The following papers were read :—

(1) Correlation between the disposition of the liver and the kidney and the form of the air-bladder in certain Siluroid Fishes of India. By Dr. S. L. Hora.

(2) The problem of k samples for Poisson Population. By Dr. P. V. Sukhatme. (Communicated by Prof. P. C. Mahalanobis).

(3) Biochemistry of *Sonti* Fermentation. By Mr. K. Rami Reddi and Prof. V. Subrahmanyan.

(4) Chemical examination of the seeds of *Cleome pentaphylla* Linn. By Mr. R. N. Misra and Dr. S. Dutt.

(5) On the electron affinity of Chlorine. By Prof. M. N. Saha and Mr. A. N. Tandon.

(6) Reflections from the Ionosphere. By Mr. R. N. Rai. (Communicated by Prof. M. N. Saha).

(7) The effect of the intensity of sound on the sound absorption co-efficient of different materials. By Mr. Hazi Gulam Mohamed. (Communicated by Prof. M. N. Saha).

9. A vote of thanks was passed to the out-going President for his activities in the cause of the Institute.

ANNUAL REPORT.

The Council of the National Institute of Sciences of India have pleasure in submitting the following report on the general concerns of the Institute for the year 1936, as required by the provisions of rule 48 (f).

Membership.

The number of Fellows on the roll of the Institute at the beginning of the year was 145 Ordinary Fellows and 7 Honorary Fellows. Eleven Ordinary and four Honorary Fellows were elected during the year in accordance with the procedure laid down in the Regulations. The Institute lost 5 Fellows by death and 6 by resignation. One Ordinary Fellow who was elected in October, 1935, did not complete the formalities and was therefore not admitted. The total number of Fellows on the roll at the end of the year is 144 Ordinary and 11 Honorary Fellows.

Accommodation.

The need for more accommodation for the offices of the Institute is already being felt and it may be necessary in the near future to approach the Royal Asiatic Society of Bengal, who have very kindly accommodated the Institute in their premises, for an additional room.

Meetings.

The First Annual General Meeting was held at the Daly College, Indore, on the 4th January, 1936. An account of the meeting was published in the *Proceedings*, Vol. II, pp. 1-2.

Two Ordinary General Meetings were held during the year, one on the 19th July, 1936, at Simla and the other at Calcutta on the 29th and 30th August, 1936. Accounts of these meetings will be found in the *Proceedings*, Vol. II, pp. 101-102 and pp. 155-157. Some of the papers read at these meetings have been published in the *Proceedings*, one is in course of publication in the *Transactions*, while others are awaiting publication in due course.

At the Ordinary General Meeting on the 29th and 30th August, 1936, a Symposium on the ' Problem of Nitrogen Supply to the Indian Soil ' was held. The papers submitted for this Symposium are being printed in the *Proceedings*.

The Council.

At the First Annual General Meeting held on the 4th January, 1936, the officers and members of Council were elected. Together with the representa-

tives of the co-operating Academies and the Indian Science Congress Association the Council was constituted as follows :—

President ..	..	. .. Sir L. L. Fermor.
Vice-Presidents	..	.. Brigadier H. J. Couchman.
		Prof. B. Sahni.
Treasurer ..	..	.. Dr. S. L. Hora.
Foreign Secretary	..	.. Prof. M. N. Saha.
Secretaries	..	.. Prof. S. P. Agharkar.
		Dr. A. M. Heron.
Members of Council	..	.. Mr. T. P. Bhaskara Shastri.
		Prof. S. S. Bhatnagar.
		Sir Bryce Burt.
		Prof. J. C. Ghosh.
		Dr. F. H. Gravely.
		Khan Bahadur M. Afzal Husain.
		Lt.-Col. R. Knowles.
		Prof. K. S. Krishnan.
		Prof. S. K. Mitra.
		Prof. J. N. Mukherjee.
		Dr. C. W. B. Normand.
		Dr. Baini Prashad.
		Prof. N. R. Sen.
		Lt.-Col. J. A. Sinton.
		Lt.-Col. S. S. Sokhey.
		Mr. C. G. Trevor.
		Prof. B. Venkatesachar.
		Mr. F. Ware.

Representatives of the Royal Asiatic Society of Bengal :—
   Additional Vice-President : Lt.-Col. R. N. Chopra.
   Additional Member of Council : Mr. C. C. Calder.

Representatives of the National Academy of Sciences, India :—
   Additional Vice-President : Prof. K. N. Bahl.
   Additional Member of Council : Prof. A. C. Banerji.

Representatives of the Indian Academy of Sciences :—
   Additional Vice-President : Prof. B. K. Singh.
   Additional Member of Council : Dr. K. V. Krishnan.

Representatives of the Indian Science Congress Association :—
   Additional Vice-President : Sir U. N. Brahmachari.
   Additional Member of Council : Mr. W. D. West.

The following changes in the Council took place during the year :—

On his retirement from India Sir Lewis Fermor resigned the office of President from the 1st April, 1936. As per provisions of Rule 44 Brigadier H. J. Couchman was appointed by the Council to be the President for the remaining period. The Council also appointed Sir Lewis Fermor to the vacant office of Vice-President. These appointments were confirmed by the Ordinary General Meeting of the Institute held at Simla on the 19th July, 1936.

At the meeting of the Council held on the 29th August, 1936, the President nominated Dr. Baini Prashad, as per Rule 47, to act as Secretary during the absence on leave out of India of Dr. A. M. Heron.

The Council appointed Dr. R. B. Lal to be a member of Council in place of Lt.-Col. R. Knowles deceased. This appointment was confirmed by the Ordinary General Meeting held on the 29th August, 1936.

The Council held eleven meetings during the year. Two important items taken up by the Council and represented to the Government of India were :—

(1) The appointment of the Assistant for India at the Kew Botanical Gardens.

(2) The method of fixing the contribution paid by countries adhering to the International Scientific Unions affiliated to the International Research Council.

The Council resolved, at its meeting held on the 8th October, 1936, to add the following additional regulation (4A) to the Regulations for the election of Ordinary Fellows :—

'The recommendations of the Sectional Committees shall be circulated to all members of Council at least 4 weeks before the date of the Ordinary General Meeting of the Institute to be held during the monsoon, and opinions invited from members so as to reach the Secretary at least 3 days before the date of the meeting of the Council.'

Sectional Committees.

The following changes were made in the personnel of the different Committees during the year :—

Physics	..	Prof. B. Venkatesachar in place of Sir C. V. Raman. (4-1-36.)
		Prof. D. M. Bose in place of Prof. S. K. Mitra as Secretary and Convener. (4-1-36.)
Physiology	..	Prof. N. N. Sengupta in place of Lt.-Col. O. Berkeley-Hill. (4-2-36.)
		Lt.-Col. R. N. Chopra as Secretary in place of Lt.-Col. R. Knowles deceased. (29-8-36.)
		Prof. W. Burridge in place of Lt.-Col. A. D. Stewart. (4-2-36.)
		Dr. R. B. Lal in place of Lt.-Col. R. Knowles deceased. (21-8-36.)
Engineering	..	Principal F. N. Mowdawalla as Secretary during the absence of Dr. E. Spencer on leave. (19-7-36.)
Geology	..	Mr. P. Evans in place of Prof. K. K. Mathur deceased. (29-8-36.)
Botany	..	Dr. W. Burns in place of Dr. F. J. F. Shaw deceased. (8-10-36.)

Additional Committees.

The following additional Committees were appointed during the year :—

A Publication Committee for 1936 consisting of the President, the Honorary Treasurer, the Honorary Secretaries and the Editor of Publications.

A sub-committee consisting of the Editor, Prof. J. N. Mukherjee and Prof. S. P. Agharkar to make concrete proposals for the distribution of the Institute's publications.

A Committee consisting of Dr. C. W. B. Normand, Prof. P. N. Ghosh and Prof. S. P. Agharkar to consider technical details in connection with the co-ordination of the investigations on Natural Illumination carried out by the various Universities in India, which the Institute had agreed to do at the request of the Government of India. Dr. S. K. Banerji was later appointed to this Committee during Dr. Normand's absence on leave.

Publications.

Four numbers of the *Proceedings* and three numbers of the *Transactions* have been published since the last annual report, and copies have been circulated to Fellows. The Council resolved at its meeting held on the 4th February, 1936, that a new volume of the *Proceedings* be started each year and that each volume of the *Transactions* should be closed when a sufficient number of pages had been printed.

The first number of *Indian Science Abstracts* for the year 1935 has also been published. It has been decided to include in this publication, abstracts of (1) all papers published in India and (2) all papers published abroad on work done in India or based on Indian material.

The completion of the first volume of this journal during 1937 will be followed by the publication of the *Annual Review of the Progress of Science in India* and thus complete the Institute's programme of publications.

Exchanges.

Seventy Societies and Institutions are now receiving the Institute's publications as presentations or in exchange. It is proposed to arrange for wider distribution of the publications of the Institute during the coming year.

Library.

Two hundred and fifty-eight books and periodicals were added to the library during the year, the greater number in exchange and a few as presentations.

Presents and Donations.

The following donations have been received during the year to the general funds of the Institute :—

(1) Rs.2,000 from His Highness the Maharaja Holkar of Indore.
(2) Rs.5,000 from Messrs. the Tata Iron and Steel Co., Ltd.
(3) Rs.2,000 from Dr. S. C. Law.

Finance.

An audited statement of accounts of the National Institute for the period from the 1st of December, 1935 to 30th of November, 1936 is submitted. The total receipts for this period amount to Rs.50,326-13-3 and the payments including purchase price of securities Rs.43,653-10-4, leaving a balance of Rs.6,673-2-11.

The following Government Securities have been purchased for the Institute during the year :—

$3\frac{1}{2}$% G.P. Notes   ..   ..   ..   Rs.10,000 (face value).

Rules.

The revised rules of the Institute incorporating the changes adopted at the last Annual General Meeting together with the Regulations for the election of Ordinary and Honorary Fellows and Sectional Committees were printed and copies have been forwarded to Fellows.

APPENDIX I.

LIST OF FELLOWS.

ORDINARY FELLOWS.

ABRAHAM, W. E. V., A.R.C.S. (I.), F.G.S., M.Inst.P.T., Senior Geologist, Burmah Oil Co., Ltd., Burma, Khodaung, Magwe, Burma. (1936).

AGHARKAR, S. P., M.A., Ph.D., F.L.S., Ghose Professor of Botany, Calcutta University, Calcutta.

AHMAD, NAZIR, M.Sc., Ph.D., Director, Indian Central Cotton Committee's Technological Laboratory, Matunga, Bombay.

AJREKAR, S. L., B.A., I.E.S., Professor of Botany, Gujerat College, Ahmedabad.

ANANDARAO, K., M.A., I.E.S., Professor of Mathematics, Presidency College, Madras.

ASH, W. C., B.Sc., M.I.C.E., A.M.I.Mech.E., Bengal Club, Calcutta.

AWATI, P. R., B.A., D.I.C., I.E.S., Professor of Zoology, Royal Institute of Science, Mayo Road, Bombay 1.

BAGCHEE, K. D., D.Sc., D.I.C., Mycologist, Imperial Forest Research Institute, Dehra Dun, U.P.

BAHL, K. N., D.Sc., D.Phil., Professor of Zoology, Lucknow University, Lucknow.

BANERJI, A. C., M.Sc., M.A., F.R.A.S., I.E.S., Professor of Mathematics, Allahabad University, Allahabad.

BANERJI, S. K., D.Sc., Meteorologist, Meteorological Office, Poona 5.

BEESON, C. F. C., D.Sc., Forest Entomologist, Imperial Institute of Forest Research, Dehra Dun, U.P.

BHASKARA SHASTRI, T. P., M.A., F.R.A.S., Director, Nizamia Observatory, Hyderabad (Deccan).

BHATNAGAR, S. S., O.B.E., D.Sc., University Professor of Chemistry, and Director, University Chemical Laboratories, Lahore.

BHATTACHARYA, D. R., M.Sc., Ph.D., Dr. ès Sciences (Paris), Professor of Zoology, Allahabad University, 7, Malaviya Road, Allahabad.

BOMFORD, Major Guy, R.E., Survey of India, Dehra Dun. (1935).

BOSE, D. M., M.A., B.Sc., Ph.D., Palit Professor of Physics, Calcutta University, 92, Upper Circular Road, Calcutta.

BOSE, G. S., D.Sc., M.B., Head of the Department of Experimental Psychology, Calcutta University, 92, Upper Circular Road, Calcutta.

BOSE, Sir J. C., Kt., C.S.I., C.I.E., M.A., D.Sc., F.R.A.S.B., F.R.S., Director, Bose Research Institute, 93, Upper Circular Road, Calcutta.

BOSE, S. N., M.Sc., Professor of Physics, Dacca University, Dacca.

BOSE, S. R., M.A., Ph.D., F.R.S.E., Professor of Botany, Carmichael Medical College, Calcutta. (1935).

BRAHMACHARI, Sir U. N., Kt., Rai Bahadur, M.A., M.D., Ph.D., F.R.A.S.B., K.I.H., Physician, Medical College Hospitals, Calcutta (Retired), 82-3, Cornwallis Street, Calcutta.

BURNS, W., D.Sc., I.A.S., Offg. Agricultural Expert, Imperial Council of Agricultural Research, New Delhi. (1935).

BURRIDGE, W., D.M., M.A. (Oxon), Professor of Physiology, Lucknow University, Lucknow.

BURT, Sir B. C., Kt., C.I.E., M.B.E., B.Sc., I.A.S., Offg. Vice-Chairman, Imperial Council of Agricultural Research, New Delhi.

CALDER, C. C., B.Sc. (Agr.), F.L.S., Director, Botanical Survey of India, and Superintendent, Royal Botanic Gardens, Sibpur, Howrah.

CHAKRAVARTI, S. N., M.Sc., D.Phil., F.C.S., Chemical Examiner to the Government of U.P. and C.P., Agra. (1935).

CHAMPION, H. G., M.A., Deputy Conservator of Forests, Haldwani Forest Division, Western Circle, United Provinces.

CHATTERJEE, G., M.Sc., Meteorologist-in-Charge, Upper Air Observatory, Agra.   (1935).

CHAUDHURI, H., M.Sc., Ph.D., D.I.C., Reader and Head of the Botany Department, Punjab University, Lahore.

CHOPRA, B. N., D.Sc., F.L.S., Assistant Superintendent, Zoological Survey of India, Indian Museum, Calcutta.   (1935).

CHOPRA, Brevet-Col. R. N., C.I.E., M.D., M.R.C.P., F.R.A.S.B., I.M.S., Director, School of Tropical Medicine, Calcutta.

CHOWLA, S., M.A., Ph.D., Professor of Mathematics, Government College, Lahore.

COUCHMAN, Brigadier H. J., D.S.O., M.C., Surveyor-General of India, Calcutta.

COULSON, A. L., D.Sc., D.I.C., F.G.S., Superintendent, Geological Survey of India, Indian Museum, Calcutta.   (1935).

DASTUR, R. H., M.Sc., Cotton Physiologist, Agricultural College, Lyallpur, Punjab.

DATTA, S., M.Sc., D.Sc., D.I.C., Professor of Physics, Presidency College, Calcutta. (1935).

DEY, B. B., D.Sc., F.I.C., I.E.S., Professor of Chemistry, Presidency College, Madras.

DHAR, N. R., D.Sc., F.I.C., I.E.S., University Professor of Chemistry, Allahabad University, Allahabad.

DUNN, J. A., D.Sc., D.I.C., F.G.S., Assistant Superintendent, Geological Survey of India, Indian Museum, Calcutta.   (1935).

DUNNICLIFF, H. B., M.A., Sc.D., F.I.C., I.E.S., University Professor of Inorganic Chemistry, Government College, Lahore.

DUTT, S. B., D.Sc., Reader in Organic Chemistry, Allahabad University, Allahabad. (1935).

EVANS, P., B.A., F.G.S., Geologist, The Burmah Oil Company, Ltd., P.O. Digboi, Assam.

FERMOR, Sir L. L., Kt., O.B.E., D.Sc., A.R.S.M., M.Inst.M.M., F.G.S., F.R.A.S.B., F.R.S., Late Director, Geological Survey of India.   C/o Standard Bank of South Africa, Cape Town.

FORSTER, Sir M. O., Kt., D.Sc., Ph.D., F.R.S., Old Banni Mantap, Mysore City.

FOWLER, Gilbert J., D.Sc., F.I.C., Consulting Chemist, Central Hotel, Bangalore.

FOX, C. S., D.Sc., M.I.Min.E., Superintendent, Geological Survey of India, Calcutta.

GEE, E. R., M.A., F.G.S., Assistant Superintendent, Geological Survey of India, Indian Museum, Calcutta.   (1935).

GHOSE, S. L., M.Sc., Ph.D., Professor of Botany, Government College, Lahore.

GHOSH, J., M.A., Ph.D., Professor of Mathematics, Presidency College, Calcutta.   (1936).

GHOSH, J. C., D.Sc., Professor and Head of the Department of Chemistry, Dacca University, Dacca.

GHOSH, P. N., M.A., Ph.D., Sc.D. (Hon.), F.Inst.P., Ghose Professor of Applied Physics, Calcutta University, 92, Upper Circular Road, Calcutta.

GLENNIE, Lt.-Col. E. A., D.S.O., R.E., Survey of India, Dehra Dun.

GRAVELY, F. H., D.Sc., F.R.A.S.B., Superintendent, Government Museum, Museum House, Egmore, Madras.

GUHA, B. S., M.A., Ph.D., Assistant Superintendent, Zoological Survey of India, Indian Museum, Calcutta.

GUHA, P. C., D.Sc., Acting Professor of Organic Chemistry, Indian Institute of Science, Bangalore.   (1935).

HADDOW, J. R., B.Sc., M.R.C.V.S., D.V.S.M., Veterinary Research Officer-in-charge of Serology, Imperial Veterinary Research Institute, Muktesar-Kumaun, U.P.

HERON, A. M., D.Sc., F.G.S., F.R.G.S., F.R.S.E., F.R.A.S.B., Director, Geological Survey of India, Indian Museum, Calcutta.

HORA, S. L., D.Sc., F.R.S.E., F.L.S., F.Z.S., F.R.A.S.B., Asst. Superintendent, Zoological Survey of India, Indian Museum, Calcutta.

HUSAIN, M. Afzal, Khan Bahadur, M.A., M.Sc., I.A.S., Principal, Punjab Agricultural College, Lyallpur, Punjab.

HUTTON, J. H., C.I.E., M.A., D.Sc., F.R.A.S.B., I.C.S. (Retd.), University Museum of Archaeology and Ethnology, Cambridge.

IYENGAR, M. O. P., M.A., Ph.D., F.L.S., University Professor of Botany, Madras University, Madras.

IYER, L. K. Ananthakrishna, Dewan Bahadur, B.A., L.T., M.D. (Hon.) Bres., Officer-in-charge of Ethnographic Survey, Mysore, Lakshminarayanapuram, P.O. Kalpathi, Palghat, S.I.

KAPUR, S. N., Ph.D., Imperial Forest Research Institute, Dehra Dun.

KICHLU, P. K., D.Sc., Professor of Physics, Government College, Lahore. (1935).

KOSHY, P. K., F.R.C.P., Professor of Anatomy, Medical College, Madras.

KOTHARI, D. S., M.Sc., Ph.D., Reader and Head of the Physics Department, Delhi University. (1936).

KRISHNA, S., Ph.D., D.Sc., F.I.C., Forest Biochemist, Imperial Forest Research Institute, Dehra Dun (U.P.).

KRISHNAN, K. S., D.Sc., Mahendra Lal Sircar Professor of Physics, Indian Association for the Cultivation of Science, 210, Bow Bazar Street, Calcutta.

KRISHNAN, K. V., M.B.B.S., L.R.C.P., D.B., D.Sc., Bacteriological Research Officer, School of Tropical Medicine, Calcutta.

KRISHNAN, M. S., Ph.D., D.I.C., Assistant Superintendent, Geological Survey of India, Indian Museum, Calcutta. (1935).

LAL, R. B., M.B.B.S., D.P.H., D.T.M. & H., D.B., Offg. Director, All-India Institute of Hygiene & Public Health, Calcutta. (1935).

LAW, S. C., M.A., B.L., Ph.D., M.B.O.U., 50, Kailas Bose Street, Calcutta. (1936).

MACMAHON, P. S., M.Sc., B.Sc. (Oxon), F.I.C., I.E.S., Professor of Chemistry, Lucknow University, Lucknow.

MAHAJANI, G. S., M.A., Ph.D., Principal and Professor of Mathematics, Fergusson College, Poona 4.

MAHALANOBIS, P. C., M.A., B.Sc., I.E.S., Professor of Physics, Presidency College, Calcutta.

MAHESWARI, P., D.Sc., Associate Professor of Botany, Agra College, Agra. (1935).

MATTHAI, George, M.A., Sc.D., F.L.S., F.Z.S., F.R.S.E., Professor of Zoology, Government College, Lahore.

MEHRA, H. R., M.Sc., Ph.D., Reader in Zoology, Allahabad University, Allahabad.

MEHTA, K. C., M.Sc., Ph.D., Professor of Botany, Agra College, Agra.

MILLS, J. P., I.C.S., Deputy Commissioner, Naga Hills, Kohima, Assam. (1936).

MITRA, S. K., D.Sc., Ghose Professor of Physics, Calcutta University, 92, Upper Circular Road, Calcutta.

MITTER, P. C., M.A., Ph.D., Ghosh Professor of Chemistry, Calcutta University, 92, Upper Circular Road, Calcutta.

MOHAMMAD, Wali, M.A., Ph.D., I.E.S., University Professor of Physics, Lucknow University, Lucknow.

MOWDAWALLA, F. N., M.A., M.I.E.E., Mem.A.I.E.E., M.I.E., 301, Frere Road, Fort, Bombay.

MUKHERJEE, J. N., D.Sc., F.C.S., Khaira Professor of Chemistry, Calcutta University, 92, Upper Circular Road, Calcutta.

NAIK, K. G., D.Sc., F.I.C., Professor of Chemistry, Baroda College, Baroda.

NARAYAN, A. L., M.A., D.Sc., Solar Physics Observatory, Kodaikanal.

NEOGI, P., M.A., Ph.D., I.E.S., Senior Professor of Chemistry, Presidency College, Calcutta. (1936).

NORMAND, C. W. B., M.A., D.Sc., Director-General of Observatories, Meteorological Office, Poona 5.

OLVER, COL. A., C.B., C.M.G., F.R.C.V.S., Animal Husbandry Expert, Imperial Council of Agricultural Research, New Delhi.

PARANJPYE, R. P., D.Sc., Vice-Chancellor, Lucknow University, Lucknow.

PARIJA, P. K., M.A., B.Sc., I.E.S., Professor of Botany, Ravenshaw College, Cuttack.

PARKINSON, C. E., Forest Botanist, Forest Research Institute, Dehra Dun. (1936).

PERCIVAL, F. G., Ph.D., F.G.S., Superintendent of Mines and Quarries, Tata Iron & Steel Co., Ltd., Jamshedpur. (1936).

PHILPOT, H. P., B.Sc. (Eng.), A.M.Inst.C.E., M.I.Mech.E., M.I.A.E., M.I.M., Principal and Jodhpur-Hardinge Professor of Technology, Engineering College, Hindu University, Benares.

PINFOLD, E. S., M.A., F.G.S., Geologist, The Attock Oil Co., Ld., Rawalpindi.

PRASAD, B. N., M.Sc., D.Sc., Ph.D., Mathematics Department, Allahabad University, Allahabad. (1936).

PRASAD, Mata, D.Sc., F.I.C., Professor of Inorganic & Physical Chemistry, Royal Institute of Science, Bombay. (1935).

PRASHAD, Baini, D.Sc., F.R.S.E., F.L.S., F.Z.S., F.R.A.S.B., Director, Zoological Survey of India, Indian Museum, Calcutta.

PRUTHI, H. S., M.Sc., Ph.D., Imperial Entomologist, Imperial Agricultural Research Institute, New Delhi.

QURESHI, Muzafaruddin, Ph.D., Professor of Chemistry, Osmania University, Hyderabad (Deccan).

RAJ, B. Sundara, M.A., Ph.D., Director of Fisheries, Chepauk, Madras. (1935).

RAMANATHAN, K. R., M.A., D.Sc., Meteorologist, Weather Office, Poona 5.

RAMDAS, L. A., M.A., Ph.D., Agricultural Meteorologist, Meteorological Office, Poona 5. (1935).

RANGASWAMI AYYANGAR, G. N., Rao Bahadur, B.A., I.A.S., Millets Specialist, Agricultural Research Institute, P.O. Lawley Road, Coimbatore, S.I.

RAO, B. Rama, M.A., D.I.C., F.G.S., Director, Geological Survey Department, Mysore State, Bangalore.

RAO, C. V. Hanumantha, M.A., Professor of Mathematics, Punjab University, Lahore.

RAY, B. B., D.Sc., Khaira Professor of Physics, Calcutta University, 92, Upper Circular Road, Calcutta. (1935).

RAY, J. N., D.Sc., Ph.D., F.I.C., Professor of Organic Chemistry, University Chemical Laboratories, Lahore. (1935).

RAY, Sir P. C., Kt., M.A., Ph.D., D.Sc., F.R.A.S.B., Palit Professor of Chemistry, Calcutta University, 92, Upper Circular Road, Calcutta.

RAY, P. R., M.A., Lecturer in Chemistry, Calcutta University, 92, Upper Circular Road, Calcutta.

ROW, Lt.-Col. R., M.D., D.Sc., I.M.S. (Hon.), 27, New Marine Lines, Bombay 1.

ROY, S. C., Rai Bahadur, M.A., B.L., Editor, ' Man in India ', Ranchi.

ROYDS, T., D.Sc., Director, Solar Physics Observatory, Kodaikanal.

SAHA, M. N., D.Sc., F.R.S., F.R.A.S.B., University Professor of Physics, Allahabad University, Allahabad.

SAHNI, B., M.A., Sc.D., D.Sc., F.G.S., F.R.S., F.R.A.S.B., University Professor of Botany, Lucknow University, Lucknow.

SARKAR, P. B., Dr. ès Sc., A.I.C., Lecturer in Chemistry, Calcutta University, 92, Upper Circular Road, Calcutta. (1935).

SEN, B. M., M.A., M.Sc., I.E.S., Principal, Presidency College, Calcutta.

SEN, H. K., M.A., D.Sc., D.I.C., Director, Indian Lac Research Institute, Namkum, Ranchi.

SEN, J. M., B.Sc., M.Ed., F.R.G.S., Assistant Director of Public Instruction, Bengal, Calcutta. (1935).

SEN, N. R., D.Sc., Ph.D., Ghose Professor of Applied Mathematics, Calcutta University, 92, Upper Circular Road, Calcutta.

SENGUPTA, N. N., Ph.D., Professor of Psychology, Lucknow University, Lucknow.

SEYMOUR SEWELL, Lt.-Col. R. B., C.I.E., M.A., Sc.D., F.R.S., M.R.C.S., L.R.C.P., F.Z.S., F.L.S., I.M.S. (Retd.), Zoological Laboratory, Cambridge. (1936).

SHORTT, Lt.-Col. H. E., I.M.S., Director, King Institute of Preventive Medicine, Guindy, Madras. (1936).

SINGH, B. K., M.A., Sc.D., F.I.C., I.E.S., Professor of Chemistry, Science College, Bankipore, Patna.

SINTON, Lt.-Col. J. A., V.C., O.B.E., M.D., D.Sc., D.P.H., D.T.M., I.M.S., c/o Lloyds Bank, 6 Pall Mall, London, S.W. 1.

SOKHEY, Lt.-Col. S. S., M.A., M.D., D.T.M. & H., I.M.S., Director, Haffkine Institute, Parel, Bombay.

SPENCER, E., D.Sc., Ph.D., F.I.C., A.R.S.M., M.I.M.M., F.G.S., Consulting Chemist, Bird & Co., Chartered Bank Buildings, Clive Street, Calcutta.

SRIVASTAVA, P. L., M.A., D.Phil., Reader in Mathematics, Allahabad University, Allahabad. (1935).

SUBRAHMANYAN, V., D.Sc., F.I.C., Professor of Biochemistry, Indian Institute of Science, Bangalore.

TAYLOR, Col. J., D.S.O., M.D., D.P.H., I.M.S., Director, Central Research Institute, Kasauli (Simla Hills).

TIRUMURTI, T. S., Rao Bahadur, B.A., M.B. & C.M., D.T.M. & H., Professor of Pathology, Medical College, Vizagapatam.

TREVOR, Sir C. G., Kt., C.I.E., President, Imperial Forest Research Institute, Dehra Dun.

UKIL, A. C., M.B., M.S.P.E., Tuberculosis Research Officer, All-India Institute of Hygiene and Public Health, Calcutta. (1935).

VENKATARAMAN, T. S., Rao Bahadur, B.A., C.I.E., I.A.S., Imperial Sugar Cane Specialist, P.O. Lawley Road, Coimbatore.

VENKATESACHAR, B., Rao Bahadur, M.A., F.Inst.P., Professor of Physics, Central College, Bangalore.

VIJAYARAGHAVAN, T., Ph.D. (Oxon), Reader in Mathematics, Dacca University, Ramna, Dacca.

VISWA NATH, B., Rao Bahadur, F.I.C., Offg. Director, Imperial Agricultural Research Institute, New Delhi.

WADIA, D. N., M.A., B.Sc., F.G.S., F.R.G.S., F.R.A.S.B., Assistant Superintendent, Geological Survey of India, Indian Museum, Calcutta.

WARE, F., F.R.C.V.S., I.V.S., Director, Imperial Veterinary Research Institute, Muktesar-Kumaun, U.P.

WEST, W. D., M.A. (Cantab.), Assistant Superintendent, Geological Survey of India, Calcutta.

WHEELER, T. S., Ph.D., F.R.C.Sc.I., F.I.C., F.Inst.P., M.I.Chem.E., Principal, Royal Institute of Science, Mayo Road, Fort, Bombay 1.

WRAIGHT, E. A., C.I.E., A.R.S.M., M.I.M.M., F.I.C., Metallurgical Inspector, Jamshedpur.

HONORARY FELLOWS.

PROF. NIELS BOHR, N.L., 15, Blegdamsvej, Copenhagen.

PROF. F. G. DONNAN, F.R.S., Director, Sir William Ramsay Laboratory, University College, London.

PROF. ALBERT EINSTEIN, N.L., Princeton University, New Jersey, U.S.A.

PROF. ALBERT HEIM, D.Sc., Zürich, Switzerland.

SIR THOMAS H. HOLLAND, K.C.S.I., K.C.I.E., D.Sc., F.R.S., Principal of the University of Edinburgh.

SIR FREDERICK GOWLAND HOPKINS, Kt., M.A., D.Sc., N.L., F.R.S., Sir William Dunn Professor of Biochemistry in the University of Cambridge.

SIR ARTHUR B. KEITH, M.D., F.R.C.S., LL.D., F.R.S., Farnborough, Kent.

SIR GUY A. K. MARSHALL, Kt., C.M.G., F.R.S., Director, Imperial Institute of Entomology, London.

LORD RUTHERFORD OF NELSON, O.M., N.L., F.R.S., Cavendish Professor of Physics, Cambridge University, Cambridge.

SIR ALBERT C. SEWARD, D.Sc., Hon. LL.D., F.R.S., Formerly Master of Downing College and Emeritus Professor of Botany in the University of Cambridge, Cambridge, 209, Cromwell Road, London, S.W. 5.

SIR CHARLES S. SHERRINGTON, O.M., G.B.E., N.L., F.R.S., Broomside, Valley Road, Ipswich, England.

APPENDIX II.

ABSTRACT PROCEEDINGS OF THE COUNCIL, 1936.

[NOTE.—These abstracts of the proceedings of the Council relate to questions dealt with which are likely to be of interest to Fellows. Routine matters and matters which are under consideration are not included.]

1. The Council addressed the Government of India regarding India's participation in the scheme of Oversea's scholarships established by the Commissioners for the 1851 Exhibition. (No. 5—13-12-35.)

(*Note*:—A reply was received from the Government of India to say that the Government have already apprised the Secretary of State of India's claim to participation in these scholarships. Both he and the Commissioners of the Exhibition are sympathetic and it is hoped that something may be done to satisfy Indian aspirations in the not distant future.

It has now been announced that one scholarship of the value of £250–300 p.a. has been sanctioned for India.)

2. The Council addressed the Government of India regarding the method of appointment of the Assistant for India at the Kew Botanical Gardens. (No. 2—4-1-1936.)

(*Note*:—A reply was received from the Government of India stating that it was decided, in order to give continuity of work in directions that call for long and undivided study, the Assistant for India at the Kew Botanical Gardens, should continue, as at present, to be a permanent officer with wide experience of India. At the same time they were of opinion that there was much to be said in favour of the deputation of young botanists to Kew to act as liaison officers for short periods and they had addressed local Governments in the matter.)

3. The Council addressed the Government of India regarding the method of fixing the contribution to be paid by countries adhering to the International Scientific Unions affiliated to the National Research Council. (No. 2—4-2-1936.)

(*Note*:—A reply was received stating that the Government of India had addressed the India Office on the subject.)

4. The Council approved the recommendation of the Finance Committee in regard to Rule 19 that relates to contributions to be paid from Fellow's subscriptions to co-operating Academies. (No. 4—24-4-1936.)

(*Note*:—This rule to be interpreted to mean that only when a Fellow has paid his annual subscription of Rs.36 to the National Institute, can he direct that Rs.12 from his subscription be paid to a co-operating Academy towards his annual subscription to that Academy.)

5. The Council considered a letter from the Government of India, enquiring whether the National Institute would be prepared to undertake the co-ordination of the investigations on natural illuminations carried out by various Universities in India and resolved to undertake the work, appointing a sub-committee consisting of Dr. C. W. B. Normand, Prof. P. N. Ghosh, and Prof. S. P. Agharkar to consider technical details in this connection. (No. 10—27-6-1936.)

(*Note*:—The letter of the Government of India refers to certain investigations on the measurements of natural illumination at various times of the day in different parts of India, which the Illumination Research Committee of the Department of Scientific and Industrial Research, London, are desirous of having carried out.)

6. The Council resolved to supply the *Indian Science Abstracts* free to Fellows and to allow 25% reduction off the published price to Fellows purchasing any of the publications of the Institute. (No. 2—29-8-1936.)

7. The annual subscriptions for the publications of the National Institute were fixed as follows :—

> *Proceedings*—Rs.10 per volume.
> *Transactions*—To be determined per part according to size and number of plates.
> *Indian Science Abstracts*—Rs.25 per volume.

8. In accordance with the Regulations the Council appointed the Sectional Committees for the year 1937. (No. 2—8-12-1936.) (See Appendix IV.)

APPENDIX III.

COMMITTEES, 1936.

SECTIONAL COMMITTEES.

(1) ' Mathematics ' Committee for Mathematics, Astronomy and Geodesy :—

Prof. A. C. Banerji ..	..	..	.. Allahabad.
Mr. T. P. Bhaskara Shastri	..	..	.. Hyderabad (Deccan).
Brigadier H. J. Couchman	..	..	.. Calcutta.
Prof. C. V. Hanumantha Rao ..	..	..	.. Lahore.
Principal G. S. Mahajani	..	..	.. Poona.
Prof. N. R. Sen ..	..	..	.. Calcutta (Secretary and Convener).

(2) ' Physics ' Committee for Physics and Meteorology :—

Dr. Nazir Ahmed	..	..	.. Bombay.
Dr. P. N. Ghosh ..	..	..	.. Calcutta.
Dr. C. W. B. Normand	..	..	.. Poona.
Prof. M. N. Saha ..	..	..	.. Allahabad.
Prof. B. Venkatesachar	..	..	.. Bangalore.
Prof. D. M. Bose ..	..	..	.. Calcutta (Secretary and Convener).

(3) ' Chemistry ' Committee for Pure and Applied Chemistry :—

Prof. S. S. Bhatnagar	..	..	.. Lahore.
Sir B. C. Burt ..	..	..	.. New Delhi.
Prof. N. R. Dhar ..	..	..	.. Allahabad.
Sir M. O. Forster ..	..	..	.. Mysore.
Prof. H. K. Sen ..	..	..	.. Calcutta.
Prof. P. C. Mitter ..	..	..	.. Calcutta (Secretary and Convener).

(4) ' Engineering Sciences ' Committee for Engineering, Metallurgy, Electro-technics and kindred subjects :—

Mr. W. C. Ash ..	..	..	.. Calcutta.
Principal F. N. Mowdawalla	..	..	.. Bangalore.
Dr. D. Penman ..	..	..	.. Dhanbad.
Mr. H. P. Philpot ..	..	..	.. Benares.
Mr. E. A. Wraight ..	..	..	.. Jamshedpur.
Dr. E. Spencer ..	..	..	.. Calcutta (Secretary and Convener).

(5) ' Geology ' Committee for Geology, Palæontology, Mineralogy and Geography :—

Sir L. L. Fermor ..	..	..	.. Calcutta.
Dr. C. S. Fox ..	..	..	.. Calcutta.
Prof. K. K. Mathur	..	..	.. Benares.
Mr. E. S. Pinfold ..	..	..	.. Rawalpindi.
Mr. B. Rama Rao	..	..	.. Bangalore.
Dr. A. M. Heron ..	..	..	.. Calcutta (Secretary and Convener).

(6) ' Botany ' Committee for Pure and Applied Botany, Forestry and Agronomy :—

Prof. S. L. Ajrekar ..	..	..	.. Ahmedabad.
Mr. H. G. Champion	..	..	.. Dehra Dun.
Prof. M. O. P. Iyengar	..	..	.. Madras.
Prof. P. K. Parija ..	..	..	.. Cuttack.
Dr. F. J. F. Shaw ..	..	..	.. Delhi.
Mr. C. C. Calder ..	..	..	.. Calcutta (Secretary and Convener).

(7) 'Zoology' Committee for Pure and Applied Zoology and Anthropology including Ethnology :—

Prof. K. N. Bahl	..	..	.. Lucknow.
Dr. C. F. C. Beeson	..	..	.. Dehra Dun.
Dr. F. H. Gravely	..	..	.. Madras.
Principal M. Afzal Husain	..	..	.. Lyallpur (Punjab).
Dr. J. H. Hutton	..	..	.. Shillong.
Dr. B. Prashad	..	..	.. Calcutta (Secretary and Convener).

(8) 'Physiology' Committee for Animal Physiology and Medical subjects :—

Sir U. N. Brahmachari	..	..	.. Calcutta.
Prof. W. Burridge	..	..	.. Lucknow.
Brevet-Col. R. N. Chopra	..	..	.. Calcutta.
Prof. P. K. Koshy	..	..	.. Madras.
Lt.-Col. R. Row	..	..	.. Bombay.
Prof. N. N. Sengupta	..	..	.. Lucknow.
Lt.-Col. J. Taylor	..	..	.. Kasauli.
Mr. F. Ware	..	..	.. Muktesar.
Lt.-Col. R. Knowles	..	..	.. Calcutta (Secretary and Convener).

EDITORIAL COMMITTEE FOR THE 'INDIAN SCIENCE ABSTRACTS'.

Dr. B. Prashad	..	..	.. General Editor.
Prof. N. R. Sen	..	..	.. ⎫
Prof. M. N. Saha	..	..	.. ⎪
Prof. J. C. Ghosh	..	..	.. ⎪
Dr. E. Spencer	..	..	.. ⎬ Associate Editors.
Dr. A. M. Heron	..	..	.. ⎪
Prof. P. K. Parija	..	..	.. ⎪
Lt.-Col. J. Taylor	..	..	.. ⎪
Mr. F. Ware	..	..	.. ⎭

APPENDIX IV.

COMMITTEES, 1937.

SECTIONAL COMMITTEES.

(1) 'Mathematics' Committee for Mathematics, Astronomy and Geodesy :—

Prof. K. Ananda Rao	..	..	.. Madras.
Prof. A. C. Banerji	..	..	.. Allahabad.
Mr. T. P. Bhaskara Shastri	..	..	.. Hyderabad (Deccan).
Lt.-Col. E. A. Glennie	..	..	.. Dehra Dun.
Prof. C. V. H. Rao	..	..	.. Lahore.
Prof. N. R. Sen	..	..	.. Calcutta (Secretary and Convener).

(2) 'Physics' Committee for Physics and Meteorology :—

Dr. Nazir Ahmad	..	..	.. Bombay.
Prof. P. N. Ghosh	..	..	.. Calcutta.
Dr. C. W. B. Normand	..	..	.. Poona.
Prof. M. N. Saha	..	..	.. Allahabad.
Prof. B. Venkatesachar	..	..	.. Bangalore.
Prof. D. M. Bose	..	..	.. Calcutta (Secretary and Convener).

(3) 'Chemistry' Committee for Pure and Applied Chemistry :—

Prof. S. S. Bhatnagar	..	..	..	Lahore.
Sir Bryce Burt	..	..	..	New Delhi.
Prof. N. R. Dhar ..	..	..	..	Allahabad.
Prof. J. N. Mukherjee	..	..	..	Calcutta.
Prof. V. Subrahmanyan	..	..	..	Bangalore.
Prof. P. C. Mitter ..	..	..	..	Calcutta (Secretary and Convener).

(4) 'Engineering Sciences' Committee for Engineering, Metallurgy, Electro-technics and Kindred subjects :—

Mr. W. E. V. Abraham	..	..	..	Khodaung (Burma).
Mr. W. C. Ash	..	..	..	Calcutta.
Mr. H. P. Philpot ..	..	..	..	Benares.
Mr. E. S. Pinfold ..	..	..	..	Rawalpindi.
Mr. E. A. Wraight ..	..	..	..	Jamshedpur.
Mr. F. N. Mowdawalla	..	..	..	Bangalore (Secretary and Convener).

(5) 'Geology' Committee for Geology, Palæontology, Mineralogy and Geography :—

Mr. P. Evans	..	..	..	Digboi.
Dr. C. S. Fox	..	..	..	Calcutta.
Mr. B. Rama Rao ..	..	..	..	Bangalore.
Mr. D. N. Wadia ..	..	..	..	Calcutta.
Mr. W. D. West	..	..	..	Calcutta.
Dr. A. M. Heron ..	..	..	..	Calcutta (Secretary and Convener).

(6) 'Botany' Committee for Pure and Applied Botany, Forestry and Agronomy :—

Dr. W. Burns	..	..	..	New Delhi.
Prof. M. O. P. Iyengar	..	..	..	Madras.
Prof. K. C. Mehta ..	..	..	..	Agra.
Prof. P. Parija	..	..	..	Cuttack.
Sir C. G. Trevor	..	..	..	Dehra Dun.
Mr. C. C. Calder	..	..	..	Calcutta (Secretary and Convener).

(7) 'Zoology' Committee for Pure and Applied Zoology and Anthropology including Ethnology :—

Prof. K. N. Bahl ..	..	..	..	Lucknow.
Dr. F. H. Gravely ..	..	..	..	Madras.
Dr. B. S. Guha	..	..	..	Calcutta.
Khan Bahadur M. Afzal Husain		..	..	Lyallpur.
Dr. H. S. Pruthi ..	..	..	..	New Delhi.
Dr. B. Prashad	..	..	..	Calcutta (Secretary and Convener).

(8) 'Physiology' Committee for Animal Physiology and Medical subjects :—

Sir U. N. Brahmachari	..	..	..	Calcutta.
Prof. W. Burridge ..	..	..	..	Lucknow.
Prof. P. K. Koshy ..	..	..	..	Madras.
Dr. R. B. Lal	..	..	..	Calcutta.
Lt.-Col. R. Row	..	..	..	Bombay.
Prof. N. N. Sengupta	..	..	..	Lucknow.
Col. J. Taylor	..	..	..	Kasauli.
Mr. F. Ware	..	..	..	Muktesar.
Brevet-Col. R. N. Chopra	..	..	..	Calcutta (Secretary and Convener)

APPENDIX V.

LIST OF PERIODICALS RECEIVED EITHER IN EXCHANGE OR AS PRESENTATION.

Indian.

Agriculture and Live Stock in India.
Annual Report of the Imperial Institute of Veterinary Research.
Biochemical and Applied Research in India.
Bulletin of the Calcutta Mathematical Society.
Bulletin of the Department of Agriculture, Mysore.
Bulletin of the Indian Central Cotton Committee.
Bulletin of the Institute of Plant Industry, Indore.
Calcutta Medical Journal.
Circulars of the Department of Agriculture, Mysore.
Electrotechnics.
General Report of the Survey of India.
Geodetic Report of the Survey of India.
Indian Forester.
Indian Forest Records.
Indian Journal of Agricultural Science.
Indian Journal of Veterinary Science and Animal Husbandry.
Indian Physico-Mathematical Journal.
Indian Medical Gazette.
Indian Zoological Memoirs.
Journal of the Indian Chemical Society.
Journal of the Indian Institute of Science.
Journal of the Indian Mathematical Society.
Journal of the Indian Medical Association.
Journal of the University of Bombay.
Madras Fisheries Department Report.
Memoirs of the Geological Survey of India.
Memoirs of the Indian Meteorological Department.
Nagpur University Journal.
Palæontologia Indica.
Proceedings of the Indian Academy of Sciences.
Proceedings of the Institute of Plant Industry, Indore.
Proceedings of the National Academy of Sciences.
Proceedings of the Physiological Society of India.
Quarterly Journal of the Geological, Mining and Metallurgical Society of India.
Records of the Botanical Survey of India.
Records of the Geological Survey of India.
Records of the Malaria Survey of India.
Records of the Mysore Geological Department.
Report of the Botanical Survey of India.
Report of the Haffkine Institute.
Report of the Indian Central Cotton Committee.
Report of the King Institute of Preventive Medicine.
Science and Culture.
Scientific Notes of the Indian Meteorological Department.
The Mathematical Student.
Transactions of the Bose Research Institute.
Transactions of the Mining and Geological Institute of India.

Foreign.

Biological Bulletin of the Marine Biological Laboratory, Woods Hole.
Bulletin of the Canada Department of Mines.
Bulletin of the Geological Survey of Uganda.
Bulletin of the International Geological Congress, U.S.S.R.
Collected Papers, Woods Hole Oceanographic Institute.
Experiment Station Records, U.S. Department of Agriculture.
Himalayan Journal.
Memoirs of the Department of Mines, Canada.
Memoirs of the Geological Survey of Uganda.

Occasional Papers of the Geological Survey of Uganda.
Papers in Physical Oceanography and Meteorology, Woods Hole Oceanographic Institute.
Report of the Department of Mines, Canada.
Report of the Geological Survey of Uganda.
Scripta Mathematica.
Transactions of the Institute of Economic Mineralogy, Moscow. ·

APPENDIX VI.

THE NATIONAL INSTITUTE OF SCIENCES OF INDIA.

Receipts and Payments Account for the year ended 30th November, 1936.

RECEIPTS.	Rs.	A.	P.
To Balance brought forward	32,168	3	0
„ Members' Admission Fees	576	0	0
„ „ Subscriptions	5,125	0	0
„ Donations	9,700	0	0
„ Contributions towards publication of 'Indian Science Abstracts'	1,250	0	0
„ Sale of Author's extra copies and publications	110	1	3
„ Sale of 'Indian Science Abstracts'	132	6	0
„ Interest on Investments	1,072	13	0
„ Miscellaneous Receipts	192	6	0
TOTAL	**50,326**	**13**	**3**

PAYMENTS.	Rs.	A.	P.	Rs.	A.	P.
By Salaries of Staff				2,069	4	3
„ Printing Circulars, Notices, etc.				182	0	0
„ „ Publications, Report, etc.				4,700	10	0
„ „ 'Indian Science Abstracts'				1,568	12	6
„ Contributions to other Science Academies under Rule 19				876	0	0
„ Postage				560	13	9
„ Stationery				177	12	3
„ Audit Fees				7	6	6
„ Purchase of Books				50	0	0
„ Miscellaneous Expenses				416	0	3
„ Bank Charges				26	3	0
„ Cash and other balances—						

Investments—

	Rs.
3½% G.P. Notes 1842/43	5,000
3½% do. 1854/55	2,000
3½% do. 1865	6,000
3½% do. 1879	2,000
3½% do. 1900/01	8,000
4% Loan 1960/70	10,000
	33,000

		Rs.	A.	P.
At cost		33,018	11	10
With Imperial Bank of India—	Rs. A. P.			
On Savings Bank Account	5,014 8 0			
On Current Account	1,643 8 5	6,658	0	5
In hand		15	2	8
		39,691	14	9
TOTAL		**50,326**	**13**	**3**

Examined with the Books and Vouchers and found in accordance therewith.

PRICE, WATERHOUSE, PEAT & CO. } *Auditors.*
Chartered Accountants,
Registered Accountants.

CALCUTTA,
5th December, 1936.

APPENDIX VII.

BUDGET ESTIMATE FOR 1936-37.

	1935-36 Estimates.	1935-36 Actuals.	Budget Estimate for 1936-37.
Ordinary Receipts.			
	Rs.	Rs.	Rs.
Subscriptions	5,200	5,125	5,000
Interest	700	1,072	1,150
Contribution for the publication of 'Indian Science Abstracts'	1,000	1,250	1,200
Sale of Publications	100	242	250
Miscellaneous	..	192	..
Contribution from General Fund	2,400	2,744	5,850
	9,400	10,625	13,450
Extraordinary Receipts.			
Admission Fee	320	576	320
Donation	..	9,700	..
	320	10,276	320
Ordinary Payments.			
Salaries and allowances	2,100	2,069	2,700
Publications	5,000	6,451	8,000
Contributions to Science Academies under Rule 19	1,000	876	1,000
Furniture	400	..	500
Postage	500	560	700
Stationery	200	177	200
Auditor's Fee	50	50	50
Miscellaneous	150	442	300
	9,400	10,625	13,450
Extraordinary Payments.			
Funding of Admission Fee and Donation	320	9,879	320

Presidential Address.

HYDERABAD, 1937.

By BRIGADIER H. J. COUCHMAN, *D.S.O., M.C.*

PROGRESS OF GEODESY IN INDIA.

I propose in this address to follow the suggestion made by our first President Sir Lewis Fermor at Indore last January that is to deal first briefly with the activities of our Institute during the past year and secondly to review the progress of the particular branch of science with which I am connected.

In reference to the National Institute, I wish first to mention the great loss that we have suffered in the retirement from service of our first President Sir Lewis Fermor. Speaking as one who has had the privilege of serving under his chairmanship on the Committee charged by the Indian Science Congress to bring this Institute into being, I can affirm without any hesitation whatever that our existence to-day is largely due to the tact, energy and judgment displayed by Sir Lewis Fermor during the whole of our proceedings.

In the name of the Council of the Institute and, I feel sure, of the whole body of Fellows I take this opportunity of thanking him for his work on our behalf.

The chief event of our Institute year has been the publication of the first part of Indian Science Abstracts. The work involved in the preparation of these abstracts is very great but it could be materially lessened if authors of scientific papers would assist by forwarding very short abstracts of them to the Institute. May I appeal for the co-operation of authors in this respect so that these abstracts may be fully worthy of this great country ?

Our other activities have been described briefly in the Annual Report and I will only refer here to the symposium held in Calcutta, at which and also at the General Meeting in Simla, many interesting papers on the productivity of the soil were read and discussed by the many experts present from all parts of India.

It is hoped that these symposia will continue to be a regular feature of the activities of our Institute.

We are deeply grateful to those who have made donations to the funds of our Institute during the year. But we are not yet self-supporting ; in 1936 nearly Rs. 6,000 has had to be spent from our capital and a similar deficit in income is expected next year. We must therefore depend on the continuance of such donations. May I appeal to the generosity of the Princes and people of India and to the Governments of India and of the Provinces to help this truly National Institute in its task of promoting and still more of co-ordinating the scientific activities of India ?

Speaking not as your President but as one who has spent over 30 years
in India, I am convinced of the necessity, in this vast country, of a National
Institute such as ours. Geographical difficulties there may be but there should
not be financial ones and I look with confidence to those who have the power
to remove them.

I now turn to the second part of this address—the Progress of Geodesy
in India.

The study of Geodesy in India has been for many years confined almost
entirely to the Survey of India department of the Government of India and
as the head of that department, it appears to me to be a suitable subject with
which I should deal. I must however explain that I have not personally been
connected with this branch of our departmental activities for many years and
I can therefore only be the somewhat halting mouthpiece of others.

Geodesy, or earth measurement, is a science with which any survey
department is intimately concerned. Without knowledge of the shape, or as
it is generally termed the figure, of the earth the mapping of any considerable
portion of the earth's surface is impossible, in the sense that the positions
of points on that surface cannot be accurately defined by their latitude and
longitude, and isolated surveys cannot be connected together.

The making of disconnected maps in India began about the middle of the
18th century but it was not until the end of that century that a start was made
to cover India with a network of accurately fixed triangulated points. This
network was primarily required for the control of surveys by preventing the
accumulation of errors, but it has been used along with triangulated arcs in
other parts of the globe to determine the figure of the earth and to this extent
its purpose was geodetic.

The year 1802, when Colonel William Lambton measured his first base
line near Madras may be taken as the beginning of the study of geodesy in
India. This study has continued with little interruption to the present time.

India has been a particularly favourable area for this study. Firstly,
with the exception of the United States of America, it is probably the largest
developed area under the control of one administration. The difficulties,
met with in other continents, in the initiation and co-ordination by different
Governments of geodetic work have consequently been absent. Secondly,
its shape provides an extremely long stretch of land area on one meridian ;
from Cape Comorin in a due northerly direction to the foothills of the Himalaya
(beyond which accurate geodetic work is hardly practicable) we have some
1,500 miles of country available. The value of this lies in the fact that prior
to the electric telegraph the accuracy of astronomical determinations of lon-
gitude was in no way comparable to those of latitude. Consequently the
earlier attempts to derive the figure of the earth were based on arcs measured
along a meridian and have only comparatively recently been extended to arcs
along a parallel. Thirdly, in the mountains to the north it possesses the most
elevated portion of the earth in close proximity to deep oceans. It has at its

PRESIDENTIAL ADDRESS.

very door ample material from which the attraction of local masses can be calculated and analysed, and theories formulated as to the structure of the earth. But it has been fortunate in another way. All these favourable attributes would have been wasted, anyhow for many years, but for the two great pioneers of geodesy in India, Colonel Lambton and Sir George Everest. These two between them controlled the early geodetic work in India for over 40 years and laid down for their successors a lasting framework on which to build.

The earliest years of geodetic study in India were spent in the measurement of base lines and arcs of triangulations and astronomical observations of latitude at selected stations along these arcs. By 1830 sufficient data had been accumulated to enable Sir George Everest to calculate his figure of the earth. The necessity for a recalculation of this figure had been apparent for some years but had obviously to wait until data were deemed to be sufficient. Until then the calculation of latitude and longitude of triangulated points, necessary for the purpose of survey, had to be based on some more or less arbitrary figure and it is known that this arbitrary figure had to be changed several times, as its unsuitability became apparent.

Everest's figure has been used for the computation of the whole of the Indian triangulation and it is therefore of interest to record that it is an oblate spheroid of which the major or equatorial semi-axis is 6377·3 kilometres with an ellipticity * or flattening of $\frac{1}{300\cdot8}$. Further investigations have shown that this spheroid is slightly too small, the modern value of the major semi-axis being about 6378·4 kilometres or some 1,200 yards greater, with an ellipticity in the region of 1/295 making the polar semi-axis about half a mile greater than Everest's.

The result of using Everest's spheroid as the reference figure for computing the elements of the Indian triangulation is that India occupies on its maps slightly more than its proper share of the earth's surface. In longitude from Baluchistan to Burma a distance of some 2,500 miles this excess is about 2,500 feet. This excess will cause no embarrassment until our neighbours carry out independent geodetic triangulation and mapping up to our common frontier where each point on the ground will then have two values of latitude and longitude, our own and our neighbours'. Until there is a prospect of this, the immense labour of republishing all Indian maps on a corrected graticule is not worth undertaking. Siam is at present our only neighbour that has carried out accurate triangulation up to the Indian border but as they have so far accepted the Indian values of latitude and longitude for their base station there is no discrepancy in maps.

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* If a = major semi-axis (equatorial)
   b = minor semi-axis (polar)
   then ellipticity $= \frac{a-b}{a}$.

DEFLECTION OF THE VERTICAL.

The geodetic method of calculating the figure of the earth is to relate the linear distances along a meridian or parallel between fixed points as determined by triangulation with the angular distance as determined by the difference of astronomical latitudes or longitudes. Such a method can only give good results if the instrument to measure the vertical angles necessary for latitude or time is truly horizontal, that is to say tangential to the spheroid of reference which is to be obtained. In the vicinity of large excesses of matter this condition is not obtained, since the mass deflects the vertical. All astronomical measures of latitude or time are therefore in error by the difference between the local vertical or direction of gravity, and the true vertical or normal to the spheroid of reference.

In calculating this spheroid therefore it is clear that stations in the vicinity of very large excesses or deficiencies of matter should be avoided.

With the elements of the spheroid of reference thus obtained the latitudes and longitudes of points fixed by triangulation are calculated and by comparing these values with those obtained astronomically a measure of the angular displacement or deflection of gravity is obtained. It must however be remembered that this measure is not absolute but will vary as the elements of the spheroid, or other figure of reference selected, are changed.

When these deflections were obtained at stations near the foot of the Himalaya and it was found, of course, that they were towards the mountains, attempts were made to connect the amount of deflection with the amount of the visible excess of matter. It was soon apparent that such connection presented great difficulties. The calculated effect of the visible excess of matter was in all cases far greater than the observed deflection. At Dehra Dun at the foot of the Himalaya, for example, the calculated deflection was 86 seconds of arc as against an observed value of 37 seconds.

The question was referred about 1853 by Sir Andrew Waugh, the Surveyor-General, to Archdeacon Pratt of Calcutta, a distinguished mathematician, and he propounded his theory of mountain compensation or what is termed isostasy to-day. I return to this theory later; it is sufficient here to remark that the theory did not completely explain the observed deflections.

OTHER GEODETIC WORK.

For nearly forty years this aspect of geodesy was not seriously pursued in India no doubt because it was realized that more data was necessary, but in 1901 Sir Sidney Burrard again directed attention to the problem in his famous paper ' On the attraction of the Himalaya mountains upon the Plumb-line '. During this interval geodetic work did not cease. India was gradually being covered with a network of primary triangulation, which is even to-day not quite complete, tidal observations were made to determine the mean sea level as a datum for the level net and the first series of pendulum observations

to determine the force of gravity were carried out in the late 1860s. The telegraphic connection of India with Europe enabled an accurate calculation of longitude to be made about 1898, incidentally shifting India some $2\frac{1}{2}$ miles west of its previous place on the globe to occupy a position which modern methods and apparatus have shown to be extremely accurate.

RECENT PROGRESS.

The present century has seen a great revival of geodetic study in India. The principal activity has been the accumulation of values of the force of gravity by means of the pendulum and of its direction by astronomical observations already referred to. In 1909 Mr. J. F. Hayford of the United States Coast and Geodetic Survey published his investigations into the theory of isostasy and this was shortly followed in India by preliminary discussions of the correctness of his theory as judged by Indian data.

Hayford's theory stated briefly was that above a certain depth below sea-level the mass in any column of unit area is the same whatever its height, or in other words that mountains and seas are compensated by underlying deficiencies and excesses of density. The theory is practically the same as that of Archdeacon Pratt to which I have referred above but is stated in a more precise way. Hayford's calculations of the depth at which compensation was complete produced the figure of about 70 miles, subsequently reduced to about 60 miles, below the sea-level surface.

Although this theory reduced materially the anomalies or differences between the theoretical and observed values of the force and direction of gravity, thus showing that a certain degree of compensation does exist, it has all along been held in India that the isostatic theory is only a partial explanation of observed results. It has been more successful in North America than in India in reducing anomalies and this may possibly indicate that, the former continent is geologically more stable. In India, however, the data accumulated seem clearly to point to the existence of deep-seated belts of excesses and deficiencies of density which have little relationship to surface geology or topography. The existence of what is probably the most marked of these belts was suggested by Sir Sidney Burrard some 30 years ago and called by him the Hidden Range, which runs across India slightly north of west through Jubbulpore. He derived this from a study of the deflections of the plumb line in Northern India and its existence becomes more and more certain as data are accumulated, not only of the direction but of the force of gravity. Such belts are inconsistent with any rigid and precise theory of isostasy such as that enunciated by Hayford which assumes that underlying densities vary only with surface heights and depths. Admittedly any theory as to the density of deep-seated masses must be put into a reasonably precise form to permit its effect on gravity to be computed with reasonable ease and one cannot condemn such a theory for its failure to explain all anomalies. The object should be to superimpose on the theory broad hypotheses which remove

so much of the residual anomaly as to enable the remainder at any station to be attributed to such local variations of density as are acceptable to geologists. Clearly any anomaly of gravity at any one station can be removed by *some* assumption of local density but this assumption will affect neighbouring stations also and may increase the anomaly there ; it may also be intrinsically impossible. Thus earlier attempts to explain by local conditions the great deficiencies of gravity in North Bihar resulted in the postulation of such a depth of light alluvium as could not be accepted.

If, however, broad assumptions of deep-seated variations of density do succeed in very materially reducing anomalies over large areas without increasing others, there is some certainty that they are correct. It is on these lines that Lt.-Colonel Glennie of the Survey of India and a Fellow of this Institute has been working for some years. After allowing for a measure of isostasy and for the effect of the Hidden Chain, he finds that the residual anomalies in the force of gravity can be further materially reduced by postulating other continuous crests and troughs in the dense sub-crust. He calls these up-warps and down-warps and has propounded theories as to their origin which are being discussed. Charts showing these warps are published in the Geodetic Reports of the Survey of India. The study of these deep-seated features, which are believed to originate some 10 to 20 miles below the surface, will, it is hoped, throw some light on seismological problems and also on so different a matter as water-logging in irrigated and other areas.

THE FORM OF THE GEOID.

Hitherto in referring to the figure or shape of the earth we have considered only a generalized figure which can be expressed in a reasonably simple mathematical form. Such a form is necessary for purposes of computation—to convert the measurements obtained by triangulation into latitude and longitude of the points fixed. By the middle of the eighteenth century it had become established that the actual shape of the sea-level surface of the earth, i.e. the geoid, could be more closely represented by a simple oblate spheroid than by a sphere. It is quite possible that an even closer approximation would be a tri-axial ellipsoid but this would involve considerable loss of computational ease.

All countries which have executed any triangulation use an oblate spheroidal figure for computation of latitude and longitude but the elements of these spheroids are not always the same. In India, as I have mentioned, the spheroid used could definitely be improved upon although the labour involved in the change would be immense. But the enormous advantages that India has derived from the early execution of triangulation has vastly outweighed the disadvantage of using Everest's spheroid and we have no cause to reproach our predecessors for this use. Had they postponed the computation of the triangulation until the elements of the spheroid had been more accurately determined the main advantage of that early start would have been lost. As

it is, India has been free from the difficulties experienced by many countries which have carried out detached surveys without a rigid framework of triangulation. Our difficulties in fact have been relegated to the frontiers where they are clearly of less importance.

But whatever spheroid is used it is evident that it cannot absolutely represent the geoid. Excesses and deficiencies of matter and of density must distort the geoid from any purely mathematical form, and it is to these distortions, or as they are usually called separations, of the geoid from the assumed spheroid that considerable attention has been recently devoted in India.

From a study of the changes in the direction of gravity along a line of stations, it is possible to compute the changes in separation that will account for them. Given a sufficiency of such stations the separations can be displayed by contours on the spheroid thus clearly showing the shape of the actual geoid.

Charts showing these contours are published from time to time in the Geodetic Reports of the Survey of India and the shape of the geoid in Peninsular India appears now to be fairly well established. More data are needed in Burma and in the Himalaya in both of which areas the geoid seems to present unusual features. Whereas in Peninsular India the separation of the geoid from the International Spheroid, the figure adopted by the International Union of Geodesy and Geophysics, varies between about 35 feet above to 40 feet below, there are indications that in Southern Burma the geoid rises to something like 140 feet above the spheroid.

In spite of the forthcoming separation of Burma from India it is hoped that it may be possible to obtain further data in this area to elucidate this peculiar feature.

The Hidden Range is clearly shown by these geoidal contours which along a line through Sambalpur, Jubbulpore, Jodhpore, and Quetta indicate a crest of between 20 and 35 feet as compared with depressions of 40 feet near Gorakhpur to the north and 10 feet near Belgaum and Madras to the south.

These geoidal contours have an intimate bearing on the heights of mountain peaks ; these have been obtained by measurements of angles of elevations from distant points, and not, of course, by spirit levelling up to the summit. While the latter method gives true geoidal heights, since the levelling instrument at each station assumes a position parallel to the geoid, the former does not. After correcting for refraction the height obtained is above the geoid at the station of observation and would only represent the true geoidal height if both station and peak were on the same geoidal contour. As this is unlikely, the heights of all distant peaks require a correction at present unknown and this fact explains the reluctance of the Survey of India to change the well-known height of Mount Everest, 29,002 feet, to a more accurately calculated but non-geoidal value of 29,141.

If I may be permitted a word of departmental glorification, I will conclude by remarking that the geodetic activities of the Survey of India have been

commended on many occasions by other countries and it is our hope that these activities will be continued for many years to come.

The study of geodesy is inevitably one involving much patience and persistence ; results are hard to come by and their practical value is often doubted. Provided liaison is maintained with geology and geophysics, geodesy must lead to a better knowledge of the earth's structure and thus extend the discoveries of these sciences.

A NOTE ON CLAY PANS IN THE BAKHARGANJ DISTRICT OF BENGAL.

By J. N. MUKHERJEE, *D.Sc.*, and M. CARBERY, *M.C.*, *M.A.*

Layers of soil impervious in various degrees to root growth and to free movements of water are often met with in the soil profile. These are generally known as pans. Several types are known. Pans of hard concretionary materials, rich in sesquioxides, humus, calcium carbonate and gypsum as also pans consisting of compact layers free from the above, such as the clay pan or the plough pan, have been met with. Ramann [1] emphasised the interrelationships between podsolisation and pan formation thus bringing it in relation to the pedogenic processes. In the *ortstein* formations studied by Ramann a cementing process is recognised. A number of subsequent investigators have supported this point of view. The plough pan, however, is observed below the soil mulch and Ramann and Ehrenberg [2] define it as the uppermost layer of the subsoil whose compactness is mainly attributed to the downward translocation of the finely dispersed material of the cultivated layer. Schlacht [3] quotes Ehrenberg as stating that plough pans are disappearing with the introduction of modern methods of cultivation but in a recent survey in Germany he finds it to be extensive. He has considered in detail the relation between pan formation and soil structure. He comments that the extensive occurrence of pans, other than those of hard concretionary materials, is not generally recognised. He finds very little dependence on the lime and humus contents, the more important factors being the clay content, the manner of mixture with the clay and the moisture content and its variations. According to him the cultivation of lucerne and potato helps the formation of such pans immediately below the cultivated layer. If destroyed, they are reported by him to be reformed within three months to two years. Hilgard [4] observed plough pans mostly in clay soils, Ramann [5] in low and sandy soils and Mayer [6] in humus sandy soils. Among the factors which promote the formation of such pans are processes which give rise to a fluid dispersed layer of the soil particles.

[1] Ramann, The evolution and classification of soils, p. 69. (English translation by C. L. Whittles.)

[2] Ramann and Ehrenberg, Die Bodenkolloide, 1915.

[3] Schlacht, *Ztschr. Pflanz. Dung.*, vol. 27A, p. 303, (1933).

[4] Hilgard, Soils, p. 186, (New York, 1916).

[5] Ramann, Bodenkunde, 1911.

[6] Mayer, *Landw. Versuchs-Stat.*, vol. 58, p. 161, (1903).

The tendency to correlate pan formation with the type and structure of the soil and the soil forming processes appears to be gaining ground. Aarnio [1] has investigated plough pan formation in relation to soil genesis. Jenny and Smith [2] postulate a sieve action principle in pan formation according to which in a soil profile the colloidal particles can migrate only in the pore channels of the soil skeleton. If the diameter of the smallest pore exceeds the greatest diameter of the clay particle, no tendency to pan formation will exist. In any other case, partial or total accumulation of colloids will take place.

In the Barisal farm it was noticed that a rich soil, which should bear a good crop of cane, failed to do so. A pan was located about 7 to 10 inches below the surface. Such pans have since been observed under water-logged or flooded conditions, under cultivated and uncultivated soils, as also under those not subject to floods or water-logging. The pan has also been observed at similar depths even where soil consists of raised earth. As paddy was mainly grown in the area the pans escaped notice. The roots of the cane grow horizontally and are unable to penetrate the pan. It is quite easy to locate the pans suitably with the help of an iron probe. It appears that these pans are extensive in the area examined. The soil is yellowish grey in colour and appears to be uniform on visual examination throughout the profile up to a depth of about 3 feet. It is free from concretionary material. A bluish layer, deeper down, has been observed in one instance. As most of the area was water-logged when the site was visited, only a preliminary examination was possible. A detailed investigation of these pans and their occurrence which, to the knowledge of the authors, have not been observed so far in Indian soils, has been undertaken.

Regarding ameliorative measures the cultivation of deep rooted plants and deep trenches facilitating drainage suggest themselves and it is intended to try them but a detailed investigation of the soil profile should precede the adoption of such measures. From such evidence and observation as have been made it would seem that if such pans were broken up, they would readily reform ; ordinary methods do not seem to be applicable.

[1] Aarnio, Om Alvtyper Geoteknisa Meddelanden No. 30, (1921). Quoted from Schlacht.
[2] Jenny and Smith, *Soil Sci.*, vol. 39, No. 5, (1935).

CORRELATION BETWEEN THE DISPOSITION OF THE LIVER AND THE KIDNEY AND THE FORM OF THE AIR-BLADDER IN CERTAIN SILUROID FISHES OF INDIA.[1]

By Sunder Lal Hora, *D.Sc.*, *F.R.S.E.*, *F.N.I.*, *Assistant Superintendent, Zoological Survey of India, Calcutta.*

(Read January 5, 1937.)

Several workers have observed and commented upon the peculiar disposition of the liver and the kidneys in certain Siluroid genera, such as *Plotosus* Cuv. & Val., *Heteropneustes* Müller (= *Saccobranchus* Cuv. & Val.), *Clarias* Linn. and *Heterobranchus* Geoffr., but, so far as I am aware, no satisfactory explanation for this peculiarity has yet been advanced. Dutta (1924), who reviewed the whole subject not very long ago, came to the conclusion that

'This unusual position of the liver and the kidney can be regarded with a very fair amount of probability to be due to the smallness of the body-cavity in which the comparatively larger liver and kidney do not find enough space and are thus thrust outside.'

Weber (1891) had previously suggested that the peculiar disposition of the liver and the kidneys in *Clarias* and *Heterobranchus* was due to the lateral expansion of the air-bladder, which carries sideways with it small lobes of the liver and the kidneys.

It is unfortunate that Bridge and Haddon's (1893) very illuminating remarks concerning the peculiarities in the disposition of the liver in certain Siluroid fishes and its correlation with the form of the air-bladder should have escaped the attention of all recent workers on the subject. According to these authors the outwardly directed peritoneal cul-de-sacs were developed for the reception of the lateral lobes of the liver as a result of the unusual lateral extension of the anterior chamber of the air-bladder and its apposition on each side to the external skin. They further stated (p. 296) that

'The possibility, however remote, that these anatomical features have no special physiological value, but are simply the necessary result of other structural modifications of undoubted utility, must also be kept in view. The relative shortness of the abdominal cavity in many Siluroids may have caused the lateral extension of the air-bladder and its consequent abutment against the external skin.'

Recently in connection with my work on the Siluroid fishes of India for a revised edition of 'Fishes' in the *Fauna of British India* series, I dissected a large number of specimens belonging to different genera of Indian Catfishes for elucidating the form of the air-bladder and the modifications undergone

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[1] Published with permission of the Director, Zoological Survey of India.

☷ Liver.　▥ Air bladder.　▨ Kidney.
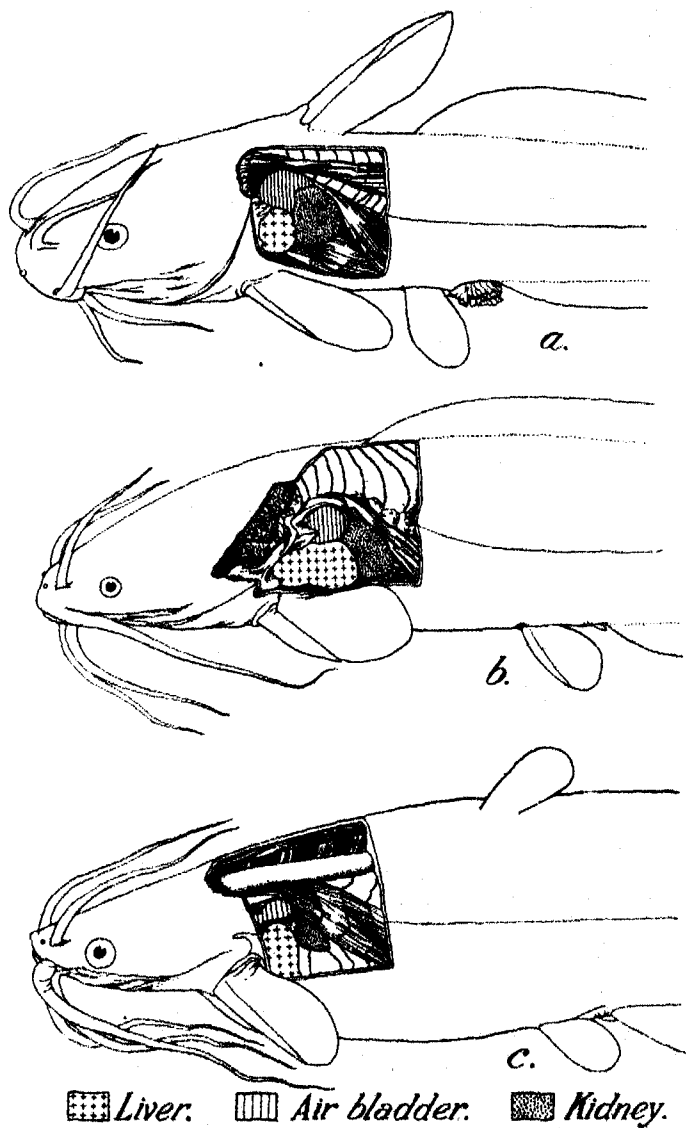
TEXT-FIG. 1.—Dorso-lateral view of the head and anterior part of the body of *Plotosus canius* Ham., *Clarias batrachus* (Linn.) and *Heteropneustes fossilis* (Bloch).

Skin in the region above the pectoral fin is removed to show the disposition of the liver, the air-bladder and the kidneys.

a. *Plotosus canius* Ham. × 1½; b. *Clarias batrachus* (Linn.) × ⅘; c. *Heteropneustes fossilis* (Bloch). Nat. Size.

by the associated skeletal structures. The disposition of the liver and the kidneys was also noted in each case, and it soon became apparent that the

chief factor that had brought about the peculiar disposition of the liver and the kidney in *Clarias, Heteropneustes,* etc. was undoubtedly the reduction of the body-cavity, while the actual formation of the extra-coelomic lobes appears to be due to the changes in shape and position of the air-bladder consequent upon the dorso-ventral flattening of the body.

In this note I trace the changes undergone by the air-bladder, the liver and the kidneys from the simple to the most highly specialized forms. As a result of the study of these types there seems little doubt that the remarkable modifications of the air-bladder, as elucidated by Bridge and Haddon in *Ailia* Gray, *Clupisoma* Swainson (=*Schilbeichthys* Bleeker), *Silonia* Swainson (= *Silundia* Cuv. & Val.), etc. are the direct result of the disposition of the liver and the kidneys and are not due to any special physiological requirements of the various forms.

For the purpose of this enquiry Günther's (1864) divisions of the Siluroid fishes into Siluridæ Homalopteræ, Siluridæ Heteropteræ, Siluridæ Proteropteræ, and Siluridæ Proteropodes are of special significance, as they are based on the external extent of the dorsal and the anal fins ; with these is also correlated the relative restriction in the size of the abdominal cavity in the various divisions. As the Siluridæ Proteropodes resemble the Siluridæ Proteropteræ in the form and extent of the anal fin, it will be sufficient to consider here the members of the first three groups only.

Among teleostean fishes, as a rule, the kidneys extend along the entire length of the dorsal wall of the abdomen, above the air-bladder : those of the two sides are partly fused with one another in the middle line. The anterior portion of each kidney is greatly dilated and, in the adult, consists of lymphatic or adenoid tissue only ; as a result, while resembling the rest of the organ in external appearance, it cannot discharge any renal function. This persistent and usually bilobed ' head-kidney ' occupies a recess of a corresponding shape lying in front of the anterior wall of the air-bladder. The liver, whose form is always closely adapted to that of the surrounding parts, lies to a greater or less extent beneath the intestinal tract.

The abdominal region in almost all Siluroid fishes is relatively short, the air-bladder extends at the sides and forms lateral cutaneous areas above the pectoral fins, the kidney is displaced from its normal position and caps the posterior part of the air-bladder, and the lateral lobes of the liver, which are displaced from their normal position, lie in peritoneal cul-de-sacs situated anterior to the lateral extension of the air-bladder.

With the forward extension of the anal fin, the body-cavity becomes still further reduced and as a result two organs, the kidney and the liver, encroach on the space usually occupied by the air-bladder. As a generalized example of the Siluridæ Heteropteræ we may consider the case of the genus *Pangasius* Bleeker which possesses a comparatively short anal fin. In very young specimens of *Pangasius pangasius* (Ham.), below 50 mm. in length, the air-bladder is extensive and its posterior portion in the form of a small hollow

knob-like protuberance lies embedded in the tissues of the kidneys ; this part
of the air-bladder represents the portion of the structure that has been squeezed
from all sides to provide more space for the kidney.   With the growth of the
fish the knob-like structure develops into a tubular cæcum and in the adult
the air-bladder consists of an anterior large, oval chamber in which the length
is greater than the breadth and a posterior long cæcum, constricted in one or
more places, extending to the base of the caudal fin.[1]   The portion of the
cæcum in the abdominal cavity, or in the earlier stages the whole of it, is
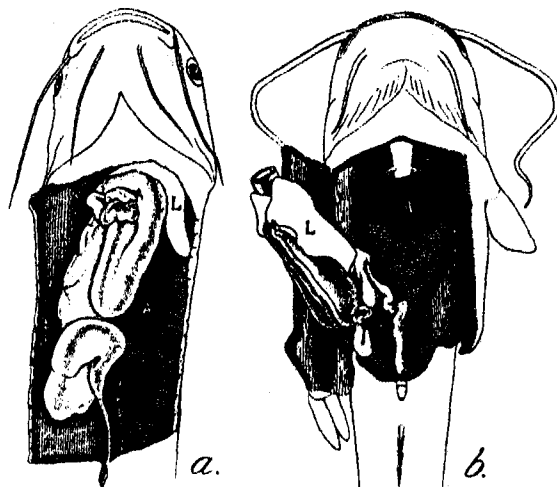
TEXT-FIG. 2.—Dissection of the visceral organs of *Pangasius pangasius* (Ham.) and
Silurus cochinchinensis Cuv. & Val., to show the disposition of the liver (L), the kidneys
(K) and the air-bladder (A).
    a. Pangasius pangasius (Ham.)× ⅔ ; *b. Silurus cochinchinensis* Cuv. & Val. Nat. Size.

surrounded by the kidneys which also extend laterally at the sides of the
anterior chamber.   This condition has no doubt resulted from the fact that as
the kidneys assumed their normal dimensions they pressed on the air-bladder for
more and more space and towards maturity the pressure on the bladder seems
to have been so great that a portion of it actually penetrated the muscles of
the caudal region to ease the pressure for space in the abdominal cavity.
Indian genera of the Siluridæ Heteropteræ may be grouped into three families—
Schilbeidæ comprising *Pangasius*, *Pseudeutropius* Bleeker, *Silonia*, *Clupisoma*,
Eutropiichthys Bleeker and *Ailia* ; Siluridæ comprising *Wallago* Bleeker,
Callichrous Ham., and *Silurus* Linn., and Heteropneustidæ [2] containing

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    [1] This also happens in certain species of the genus *Cryptopterus* Bleeker (Family
Siluridæ).
    [2] Regan (1911) included this in the family Clariidæ, but I (1936 a) have given reasons
elsewhere that this genus is closely related to the Siluridæ and on account of its special
features should be regarded as the type of a distinct family.

Heteropneustes. The last two families and the Siluridæ Homalopteræ are considered first.

According to the general body-form, the Siluridæ may be divided into two sections, (i) in which the body is greatly compressed, such as *Wallago* and *Callichrous,* and (ii) in which the trunk region is at least moderately depressed, such as *Silurus.* In the first two genera the air-bladder is co-extensive with the abdominal cavity ; it is deeper than broad and the lateral walls of its anterior part lie just beneath the skin. The kidneys cap a consider-
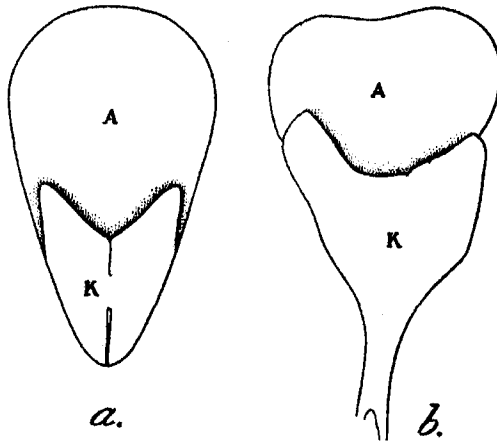
TEXT-FIG. 3.—Air-bladder (A) and Kidneys (K) of *Wallago attu* (Bloch) and *Silurus cochinchinensis* Cuv. & Val.

a. *Wallago attu* (Bloch). × 1⅘ ; b. *Silurus cochinchinensis* Cuv. & Val. × 2⅘.   ·

able part of its posterior portion. In *Silurus,* however, the air-bladder occupies only one-third of the length of the abdominal cavity and is broader than long. It is thick-walled, thereby showing that its utility is partly lost. The kidneys are fairly extensive and are broadened anteriorly into a cup-shaped structure in which is lodged the posterior part of the bladder. The liver (text-fig. 2 *b*) is also very extensive, especially on the left side, and lies closely pressed against the air-bladder. In *Olyra* McClelland, an aberrant genus for which I (1936) have proposed a separate family, the air-bladder, though very similar to that of *Silurus,* is still further reduced. The disposition of the liver and the kidneys is very similar to that of *Silurus,* except that the kidneys now extend almost to the areas of the skin beneath which lie the lateral walls of the air-bladder.

If a *Silurus*-like fish were to become greatly depressed, the space inside its body-cavity will be correspondingly reduced, and the forward push of the kidneys would result in the air-bladder assuming a transverse, tubular form, while to combat the forward thrust of these organs the bony elements would be developed in front of the air-bladder. Even in *Olyra* the beginnings of a
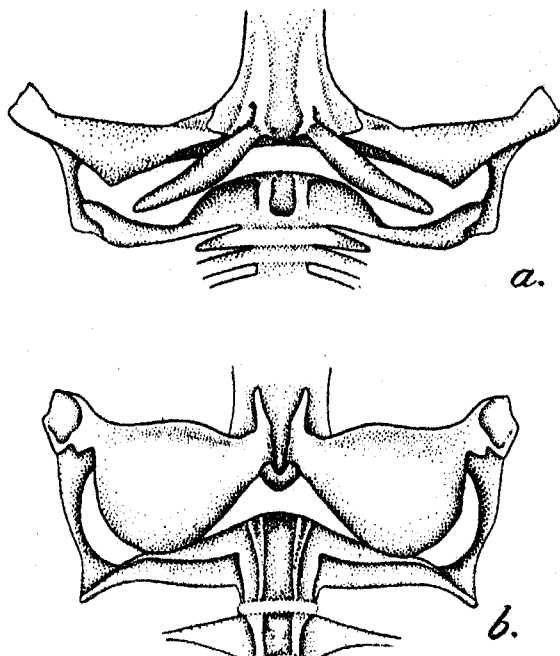
TEXT-FIG. 4.—Air-bladder (unshaded portion) and associated skeletal structures in *Clarias batrachus* (Linn.) and *Heteropneustes fossilis* (Bloch).

a. *Clarias batrachus* (Linn.). × 4 ; b. *Heteropneustes fossilis* (Bloch). × 4.

protective bony capsule are to be seen in the wing-like expansions of the transverse processes of the complex vertebra which partly envelop the anterior
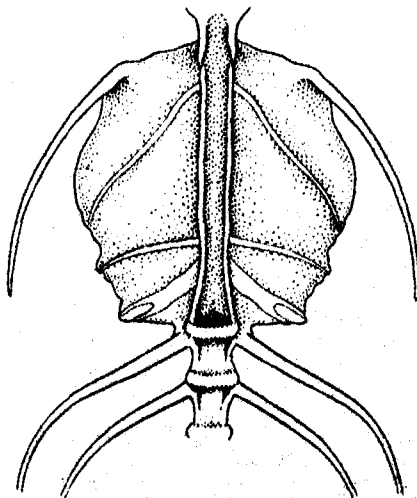
TEXT-FIG. 5.—Wing-like expansions of the transverse processes of the complex vertebra in *Olyra longicaudata* McClelland. × 7.

part of the bladder. In the hypothetical case taken above, the forward growth of the kidneys, however, would be checked by the air-bladder and its bony capsules. The liver would also be able to extend laterally along with the bladder and come to lie ventral to it, beneath the skin in small extra-coelomic cul-de-sacs. Owing to the space required for the liver, anterior to the bony elements, the 'head-kidneys' would also be displaced from their normal position and pushed outwards round the posterior part of the air-bladder. Such series of changes have, in my opinion, brought about the peculiar dis-
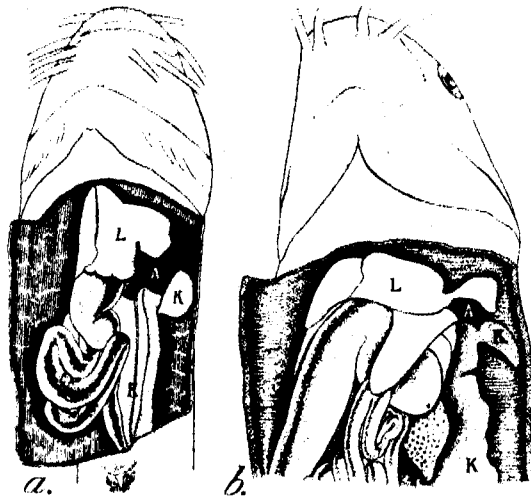
TEXT-FIG. 6.—Dissection of the visceral organs of *Plotosus canius* Ham. and *Heteropneustes fossilis* (Bloch), to show the disposition of the liver (L.), the air-bladder (A) and the kidneys (K).

a. Plotosus canius Ham. × ⅓ ; *b. Heteropneustes fossilis* (Bloch). × 1¼.

position of the liver and the kidneys in *Heteropneustes* (text-fig. 1 c).

It is clear from the above that with the reduction of the body-cavity the kidneys encroach upon the space normally occupied by the air-bladder and thus set up a series of changes which result ultimately in the extrusion of small lobes of the liver and the kidneys into extra-coelomic spaces. With regard to the displacement of the liver, Bridge and Haddon have already noted (1893, p. 226) that

'In nearly all Siluroids the lateral growth of the air-bladder, and the intimate relation of its outer walls to the lateral cutaneous areas, have led to the displacement of the lateral lobes of the liver and their enclosure within peritoneal cul-de-sacs, a condition which sometimes persists even in cases where the air-bladder has undergone partial atrophy.'

Dutta (1924) showed that the extra-coelomic kidney in *Clarias* and *Heteropneustes* is devoid of any uriniferous tubules, Malpighian capsules and glomeruli and concluded that these facts 'definitely and clearly indicate that this portion of the kidney is a non-functional and degenerate organ '. Evidently he appears to have overlooked the fact already referred to above (*supra*,

p. 33) that in all teleostean fishes the anterior end of the kidney is usually converted into adenoid or lymphatic tissue, and though resembling the rest of the organ, it does not discharge a renal function. It has also been noted above that the ' head-kidney ' only is pushed outwards into the extra-coelomic sacs. The modified lymphatic tissue of the ' head-kidney ' probably discharges some very vital functions, as in spite of the lack of space for the extension of the kidney proper, it is being retained as a fairly large structure. In this connection it is very significant to note that the extra-coelomic portion of the liver has probably undergone no degeneration, as it was found by Dutta to be histologically exactly similar to the normal portion of the liver inside the body-cavity.

The Siluridæ Homalopteræ may next be considered. These forms, besides showing an antero-posterior reduction of the body-cavity, are characterized by the greatly depressed form of the body, similar to that of *Heteropneustes*. The three Indian genera of this division—*Chaca* Gray, *Plotosus* and *Clarias*, are now regarded as belonging to three different families which probably have no genetic affinity with one another. *Chaca*, with a greatly depressed form, has a relatively much more spacious body-cavity ; the disposition of the air-bladder, the liver and the kidneys in this genus is similar to that of *Silurus*. In *Plotosus* (text-fig. 1 *a*) the bladder is considerably reduced, is broader than long and its lateral walls lie beneath the skin. As usual the kidneys cap its posterior portion, while lobes of the kidneys (presumably the ' head-kidneys ') extend laterally along the bladder and come to lie beneath the skin. The liver also caps the anterior part of the bladder and sends out broad lateral flaps, which in younger specimens come to lie beneath the skin. In *Clarias* (text-fig. 1 *b*) the disposition of the liver, the kidneys and the air-bladder is very similar to that described above for *Heteropneustes*. As in the latter genus the air-bladder of *Clarias* also is in the form of a fairly wide, horizontal tube which is partially enclosed in bone (text-fig. 4 *a*).

So far I have considered the modifications undergone by the air-bladder, the kidneys and the liver consequent upon the reduction of the abdominal cavity both antero-posteriorly as well as vertically. During these changes the organs could only extend laterally into the muscles of the anterior region of the body wall. In the Schilbeidæ the reduction of the body-cavity is effected through the compression of the body, resulting in the specialized genera of the family assuming a Clupeid form in which the body is greatly compressed and the ventral surface almost forms a sharp keel. *Pangasius*, to which a reference has been made above (*supra*, p. 3), is, in my opinion, a generalized representative of the family Schilbeidæ, so we may start our series with that genus. In the course of evolution this genus, as I have shown elsewhere,[1] gave rise to

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[1] In my revision of the Indian Schilbeidæ to be published in the *Records of the Indian Museum* for 1937 I have discussed the systematic position of *Pangasius* and shown the evolution of most of the other genera from this generalized type.

very diverse forms. Some of these are discussed below. In *Pseudeutropius*, as also in *Eutropius* Müll. & Trosch., *Schilbe* Cuv. and *Silurandon* Bleeker of Africa, the air-bladder is fairly extensive, in some forms it is co-extensive with the abdominal cavity while in others it is of the same nature as in *Silurus*, *Olyra*, etc., and the disposition of the liver and the kidney is also similar to that of either *Wallago* or *Silurus* (*vide supra*, p. 35). In certain species the lateral walls of the anterior portion of the bladder come to lie just beneath the skin and are to be distinguished externally as translucent, blister-like areas above the pectoral fins ; while in other forms the bladder is fairly thick-walled and occupies only one-quarter to one-half the length of the body-cavity.

As the body-cavity became more and more reduced antero-posteriorly, as also laterally, important adjustments occurred in the disposition of the air-bladder, the kidneys and the liver. In *Clupisoma*, for instance, the normal kidneys not only pushed the air-bladder forwards but are also extended over its ventral surface. The ' head-kidneys ', which were displaced from their normal
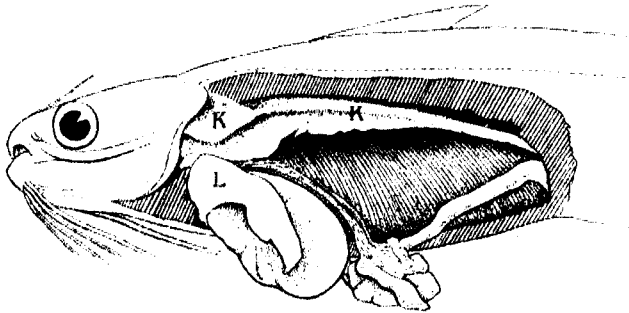
TEXT-FIG. 7.—Dissection of the visceral organs of *Clupisoma garua* (Ham.), to show the disposition of the liver (L) and the kidneys (K). × 1½.

position, form lateral lobes at the sides of the kidneys within the coelomic cavity. Further, owing to the great reduction of the body-cavity in its ventral portion the liver was displaced into the dorsal portion of the cavity, and presses the air-bladder from below. Under these circumstances the air-bladder of *Clupisoma* became greatly reduced and flattened. In some other genera, however, such as *Silonia*, *Eutropiichthys* and *Ailia*, the liver appears to have exerted more pressure on the air-bladder from below and the normal kidneys pushed it from behind so that it became greatly reduced and its central area became more or less solid or disappeared altogether. In young specimens of *Silonia* the air-bladder consists of a small, rounded structure with the normal kidneys capping its posterior part and the liver making a fairly broad depression in its middle. With the growth of the fish the kidneys extend forwards and the liver impinges on the air-bladder from below with the result that the bladder ultimately becomes divided into two portions, slightly united anteriorly, which come to lie in deep recesses formed in the transverse processes of the

complex vertebrae. The 'head-kidneys' are in their normal position anterior
to the air-bladder. In *Eutropiichthys* the air-bladder is tubular and horse-
shoe-shaped, but its posterior part is covered by the kidneys which provide a
wide depression on the ventral surface for the liver. Even here the 'head-
kidneys' are in their normal position. In *Ailia*, the most highly compressed
fish among the Indian Schilbeidæ, the tubular, and horse-shoe-shaped air-
bladder is covered anteriorly by the 'head-kidneys' and posteriorly by the
normal kidneys which extend on the sides and occupy a considerable area in
front of the posterior boundary of the air-bladder. Only a small portion of
the air-bladder, however, is seen between the kidneys. The anterior part of
the air-bladder is covered by a bony structure which now separates the 'head-
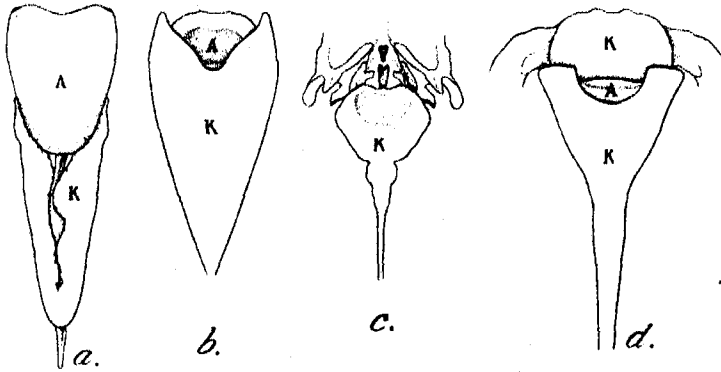
TEXT-FIG. 8.—Disposition of the kidneys (K) and the air-bladder (A) in certain Indian
genera of the Schilbeidæ.

a. Pangasius pangasius (Ham.), half-grown specimen with a portion of the air-bladder
extending into the caudal region. × ⅔ ; *b. Silonia silundia* (Ham.), young specimen, 135
mm. in total length. × 1¼ ; *c. Eutropiichthys vacha* (Ham.), young specimen, 140 mm. in
total length. × 1¼ ; *d. Ailia coila* (Ham.), half-grown specimen, 88 mm. in total length. × 3¼.

kidneys' from the vital part of the bladder itself. Though *Ailia* and
Eutropiichthys are probably not very closely related forms, the similarity in
the structure of their air-bladder appears to have been induced by similar
circumstances.

Reference may here be made to an extra-Indian form, the Siamese genus
Platytropius Hora,[1] as it exhibits remarkable modifications. I have shown
that its air-bladder is greatly flattened dorso-ventrally and has assumed a
more or less leaf-like form.[2] The kidneys in this case lie in their normal
position dorsal to the air-bladder but are greatly flattened. The 'head-
kidneys' are situated in their normal position.

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[1] Genotype : *Pseudeu'ropius siamensis* Sauvage. This new genus will shortly be de-
scribed in the *Journal of the Siam Society*, Natural History Supplement.

[2] In *Osteogeniosus*, in which the air-bladder is more or less of the same type as that
of *Platytropius*, the disposition of both types of kidneys is also similar.

From the modifications detailed above it is clear that for the peculiar disposition of the liver and the kidneys the initiative is provided by the forward extension of the caudal region and the consequent reduction of the space in the body-cavity. The necessary adjustments for the accommodation of the various organs in the reduced space are effected in various ways, mainly depending on the form of the body-cavity. In dorso-ventrally flattened forms there is a lateral extension of the organs, and the lateral portions of the air-bladder, the liver and the kidneys all come to lie just beneath the skin,
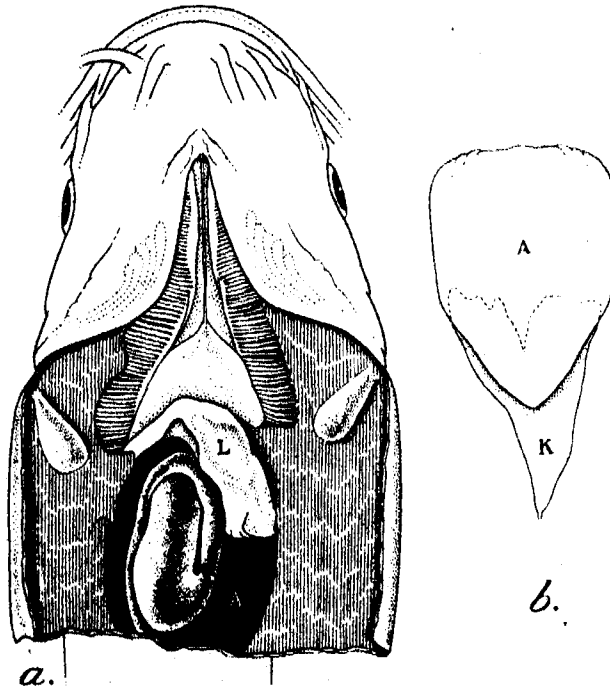
TEXT-FIG. 9.—*Platytropius siamensis* (Sauvage).
a. Dissection of the visceral organs to show the disposition of the liver (L) and the air-bladder (A). × 1½; *b.* Disposition of the air-bladder (A) and the kidneys (K). × 5¼.
Dotted line represents the extent of the kidneys dorsal to the air-bladder or the portion of the kidneys covered by the air-bladder on the ventral surface.

as in *Plotosus, Clarias, Heteropneustes*, etc. If, on the other hand, the body is compressed from side to side the kidneys may lie in their normal position under a very much flattened air-bladder as in *Platytropius*, or may gradually push the air-bladder forwards till the latter, unable to expand laterally, becomes reduced to form a narrow horse-shoe-shaped tube, as in certain genera of the Schilbeidæ. I am of opinion that no special physiological value can be attached to these anatomical features which are obviously the result of a morphological adjustment consequent upon the reduction of the abdominal cavity. The air-bladder does not appear to be an organ of primary importance in the economy

of life of these fishes, and whenever more space is required, either for the liver or the kidneys, nature provides it at the expense of the air-bladder.

SUMMARY.

The present views with regard to the peculiar disposition of the liver and the kidney are given and it is indicated that though no satisfactory solution of the problem has yet been suggested, the shortening of the body-cavity has been assumed to be the main cause both by Bridge and Haddon and Dutta, whereas Weber attributed the peculiarities to the lateral expansion of the air-bladder.

Günther's system of classification of the Siluroid fishes has been followed in this article as a matter of convenience. Generally in the Siluroid fishes the body-cavity is small and the liver and the kidneys are somewhat displaced from their normal position. In Siluridæ Heteropteræ, in which the dorsal fin is short and the anal fin long, the changes in the form and disposition of the air-bladder, the liver and the kidneys are dealt with in a progressive series from a primitive form like *Pangasius* to such highly specialized genera as *Clupisoma*, *Eutropiichthys* and *Ailia* of the Schilbeidæ and *Heteropneustes* of the Heteropneustidæ. The changes due to compression and depression of the body are shown to be of a very different nature ; in the Schilbeidæ, in which the body is compressed, the air-bladder becomes greatly reduced and in extreme cases forms a horse-shoe-shaped tube, the functional kidneys may, wholly or partly, extend over the reduced air-bladder, while the liver is pushed upwards and presses on the air-bladder. In Heteropneustidæ, in which the body is depressed, the air-bladder assumes the form of a fairly wide transverse tube which extends laterally to the skin ; along with the air-bladder, the liver and the kidneys also extend laterally and come to lie beneath the skin on the two sides of the air-bladder. In the three Indian genera of the Siluridæ Homalopteræ, *Chaca*, *Plotosus* and *Clarias*, the body is greatly depressed ; their air-bladder, kidneys and liver show a series of changes leading to the condition described in the Heteropneustidæ. Reference is also made to the modifications observed in *Platytropius*, a Siamese genus.

It is concluded that the main cause of these modifications is the shortening of the body-cavity and the subsequent adjustment of the organs within the short space available.

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CHEMICAL EXAMINATION OF THE SEEDS OF *CLEOME PENTAPHYLLA* LINN. PART I: ISOLATION OF CLEOMIN.

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(Read January 5, 1937.)

Cleome pentaphylla Linn. or *Gynandropsis pentaphylla* DC. is a plant belonging to the natural order Capparideæ and is called *Hurhur* in Hindustani, *Hurhuriya* in Bengali, and *Surjävarta* or *Arkapushpika* in Sanskrit. It is a common weed throughout the warm parts of India and is very common in Ceylon in waste and in cultivated land.

As regards its medicinal properties it has been used in Indian medicine for a very long time and the seeds, leaf, and the roots are all made use of. Sir W. Jones thinks that it promises antispasmodic virtues and according to Dr. Wright the bruised leaves are rubefacient and vasicant. The expressed juice is popularly known as an application for otalgia, both in India and in the West Indies, where also the plant is indigenous. The seeds are anthelmintic and rubefacient and are internally used for expelling round-worms and externally as a counter-irritant. The juice of the leaves is used in otalgia and the leaves are put on boils to prevent formation of pus (Kirtikar and Basu, *Ind. Med. Plants*, 1918, I, 101). A decoction of the roots is said to be a mild febrifuge.

Regarding the chemical properties of this highly interesting drug practically nothing is known. Hooper found that ‘ the seeds yield to ether about 25% of a thick, greenish, drying oil, having an Acid Value of 6·4, Saponification Value 194·6, Iodine Value 119·5 ’ (*Ann. Rept. Indian Museum, Industrial Section*, 1908-09). The present authors made a systematic examination of the seeds, as a result of which the active principle has been isolated in a state of purity (0·25%) ; a fixed oil (22·0%), which will be described in a subsequent paper ; tannins (1%) and reducing sugars. The active principle has been named *cleomin* after the generic name of the plant from which it has been derived.

Cleomin has a molecular formula $C_{17}H_{14}O_7$. It gives a dull reddish-yellow colour with alcoholic ferric chloride, but no precipitate with lead acetate, basic lead acetate, silver nitrate or mercuric chloride. It forms a mono-acetyl and a mono-benzoyl derivative. The mono-methyl derivative could not be obtained in a crystalline condition. Thus there must be one oxygen atom as an hydroxyl group. Cleomin did not show the presence of any aldehydic or ketonic groups, since it does not react with hydroxylamine, phenylhydrazine, or semi-carbazide ; nor does it reduce Fehling's solution.

Tollen's reagent was gradually reduced by it. It dissolves in alcoholic caustic potash on warming to a beautiful yellow coloured solution, and is reprecipitated on acidification. It gives no colour with alcoholic potassium nitroprusside. These reactions, which are shared by some of the natural lactones, at once place cleomin in the class of $\Delta^{\alpha\,:\,\beta}$ unsaturated lactones, which were first of all studied by Thiele (*Ann.* 1901, *319*, 155), and more exhaustively by Jacobs and collaborators (cf. also Späth and collaborators, *Ber.* 1931, 2203; 1933, 749, 914, 751). Thus out of seven oxygen atoms three have been accounted for, one in the hydroxyl group and two in the lactone group.

In this connection it is very interesting to note that from a series of Indian medicinal plants which are reputed to possess anthelmintic properties substances of the nature of a lactone have been isolated. Thus, Sen isolated corchoritin from jute seeds (*J.I.C.S.* 1931, *8*, 651); Dixit and Dutt, marmelosin from *Aegle Marmelos* (*J.I.C.S.* 1930, *7*, 759); Agarwal and Dutt, α-elaterin from *Citrullus Colocynthis* (*Proc. Acad. Sc. U.P.*, 1935, *3*, 250); and Agarwal and Dutt, cuscutalin from *Cuscuta Reflexa* (*J.I.C.S.* 1935, *12*, 384, 586). However, the physiological examination of cuscutalin and cleomin which is in progress in our laboratories will probably throw more light on this aspect of the problem. Further work to elucidate the constitution of cleomin is in progress and will be communicated shortly.

EXPERIMENTAL.

2 kg. of a genuine sample of *Cleome pentaphylla* Linn. was obtained from the neighbourhood and dried completely in shade. It was then crushed finely. A sample when burnt completely in a porcelain dish left 8·2% of a brownish white ash consisting of 18·2% water soluble and 81·8% water insoluble portions. The following inorganic elements and radicles were detected in the ash :—

Na, K, Mg (traces), Ca, NO_3, PO_4, and silica.

In order to obtain an idea of the soluble portions of the drug a sample of the dried and crushed material was exhaustively extracted in a Soxhlet's apparatus using various solvents successively, when the following amounts of extracts dried at 100°C. were obtained :—

Benzene extract : 22%, consisting of a light green oil.

Chloroform extract : 1·35% consisting of a greenish syrupy gummy material.

Ethyl acetate extract : 3·0%. A dirty brown extract was obtained giving a bluish colour with ferric chloride and a copious precipitate with lead acetate.

Acetone extract : 2·2%, a brownish sticky extract having properties similar to the alcoholic extract.

Alcohol extract : 4·8%, consisting of a brown semi-solid material which on keeping deposited minute crystals of a characteristic lens shape. The extract was found to contain tannins, and reducing sugars besides, and gave

a green colour with alcoholic ferric chloride, reduced Fehling's solution, gave a flocculent precipitate with alcoholic lead acetate and basic lead acetate.

The main bulk of the powdered material was then extracted in a large extraction flask with benzene repeatedly, till a portion of it was found to leave no oily residue on complete removal of the solvent by evaporation. The oil thus obtained amounted to 445 gms. and was worked up separately. The defatted mass was freed completely from benzene and then extracted exhaustively with boiling ethyl alcohol.

Isolation of Cleomin.—The various alcoholic extracts of a light brown colour were combined together and concentrated whereby a syrupy residue was obtained. This on standing for about three weeks deposited cleomin as a pale yellow crystalline powder melting with decomposition irregularly between 220–227°C. This was filtered from the syrupy mother liquor over a pump with a good suction. The crude stuff thus obtained was then crystallized from a very large quantity of alcohol. The final purification was effected by recrystallizing it several times from aqueous pyridine, from which it was obtained in clusters of needles. These under a powerful microscope revealed plates with hexagonal ends. Cleomin can also be crystallized from alcohol in characteristic lens-shaped crystals. In this manner 2·8 gm. of the finally purified material of a very light yellow colour was obtained. On heating it changes colour between 230–240° to dark grey, shrinks at 243°C., and melts completely with decomposition at 245-246°C.

Properties of Cleomin.—Cleomin is a light yellow crystalline substance soluble in pyridine, very little soluble in ethyl and methyl alcohols, acetone, ethyl acetate, and glacial acetic acid; totally insoluble in benzene, ligroin, petroleum ether, chloroform, carbon tetrachloride, carbon disulphide, and water. It dissolves in hot alcoholic caustic potash and caustic soda solutions giving a beautiful yellow coloration from which a white precipitate is thrown down on acidification. It decolorizes bromine water and a dilute solution of potassium permanganate. It gives a positive Salkowsky's reaction, i.e. a solution of cleomin in pyridine and conc. sulphuric acid gives a red and finally a green coloration. In conc. sulphuric acid it dissolves giving a light pale yellow colour, which on warming gradually turns from various shades of reddish-yellow to green and on heating further changes to a deep bluish-violet colour with greenish fluorescence and finally a deep violet; from the solution a flocculent precipitate separates on addition of excess of water. This reaction is very sensitive and can be utilized for detecting minute quantities of cleomin. Whereas a neutral solution of potassium permanganate is decolorized only slowly, it is immediately decolorized in the alkaline state. Cleomin is not acted upon by hydrochloric acid while cold, hot, or even boiling. In nitric acid it is soluble to a deep red coloured solution with some effervescence. From the solution a white flocculent deposit is thrown down on dilution with water. With Tollen's reagent colour develops on warming and passes gradually through orange-yellow, orange, grey, to finally black with separation of metallic

silver. It does not give a positive reaction with sodium nitroprusside, nor a positive Keller-Killiani reaction. It gives no precipitates with lead acetate, basic lead acetate, silver nitrate, or mercuric chloride. (Found: C, 61·55, 61·38, 61·42; H, 4·91, 4·70, 4·53; M.W. (Rast's camphor method) 353, 358, 320; $C_{17}H_{14}O_7$ requires C, 61·8; H, 4·2; M.W. 330.)

For the determination of the molecular weight we were confronted with unforeseen difficulties. The ordinary cryoscopic and ebullioscopic methods were rendered useless on account of the exceedingly small solubility of the substance in almost all organic solvents and its total insolubility in most of them. It was only the Rast's camphor method which gave a series of concordant values.

Mono-acetyl Cleomin.—Cleomin (1·0 gm.) was suspended in acetic anhydride (5 cc.) along with fused sodium acetate (2 gm.), and the mixture refluxed over a sand bath for three hours. The resulting mass was then poured into water when a thick oily layer deposited at the bottom. The oil solidified on repeated washing with water and standing. The colourless amorphous mass thus obtained was filtered and recrystallized from 80% acetic acid. In this manner it was obtained in soft colourless needles of m.p. 175-76°C. It was found to be easily soluble in methyl alcohol, ethyl alcohol, glacial acetic acid, acetone, and ethyl acetate, and was insoluble in benzene, petroleum ether, chloroform and water. It gave no colour with alcoholic ferric chloride. (Found: C, 61·11, 61·23; H, 5·14, 5·01; $C_{19}H_{16}O_8$ requires, C, 61·3, H, 4·30.)

Mono-benzoyl Cleomin.—Cleomin (·8 gm.) was dissolved in pyridine (10 cc.) and benzoyl chloride added drop by drop with continuous shaking, till in sufficient excess. The red coloured mass was then poured into water and treated with sodium bicarbonate to remove the benzoic acid formed. The resulting oily layer solidified on long standing and crumbled to a fine powder of a brick-red colour. On crystallization from methyl alcohol it deposited colourless clusters of nodules. These on heating shrink at 179° and melt completely at 182-83°C. (Found: C, 66·1, 66·16; H, 4·8, 4·92; $C_{23}H_{18}O_8$ requires C, 66·36, H, 4·15.)

Mono-methyl Cleomin.—Cleomin (·64 gm.) was dissolved in 10% aqueous caustic soda (50 cc.) and treated with excess of dimethyl sulphate in instalments keeping the solution always alkaline. On shaking the mixture a greyish black oil separated which failed to solidify. It was repeatedly extracted with chloroform but no crystalline derivative could be obtained.

Saponification of Cleomin.—Cleomin (·2730 gm.) was dissolved in 30 cc. of $\frac{N}{1·92}$ alcoholic caustic potash and refluxed for 2 hours. The resulting bright yellow coloured solution was then titrated with standard hydrochloric acid in order to estimate the amount of unreacted alkali. A blank experiment was done in order to minimize the error. The neutralized solution on further addition of acid deposited a white crystalline powder which on recrystallization from aqueous methyl alcohol gave microscopic needles of M.P. 240°C. This

was identified to be cleomin. A mixed melting point with the authentic sample remained undepressed at 240°C. (Found, Neutralization Value 103, calc. M.W. 309 ; $C_{17}H_{14}O_7$ requires, Neut. Value 110, M.W. 330.)

The mother liquor after separation of cleomin as described above was then diluted with ethyl alcohol and treated with excess of an alcoholic solution of lead acetate. The resulting yellow precipitate was filtered and washed with alcohol and decomposed in alcoholic suspension by hydrogen sulphide. The filtrate from the precipitated lead sulphide gave a tarry dark coloured mass which answered to all reactions of tannins.

The filtrate from the lead salt was concentrated after freeing it from excess of lead, and on standing yielded a further crop of cleomin crystals. This was purified in the usual manner. The mother liquor from this gave all reactions of reducing sugars and an osazone was prepared. This melted at 203°C., showing the presence of glucose in the seeds.

Symposium on the Problem of Nitrogen Supply to Indian Soils.

The Council of the National Institute of Sciences in India considered that a symposium on the nitrogen problem of Indian soils would be very opportune as it would focus attention on the problems for scientific investigation and on the progress already achieved and would also stimulate further work on this most important problem of practical agriculture. Prof. J. N. Mukherjee was requested by the Council to arrange the symposium which was held in Calcutta on the 29th and 30th of August, 1936. Brigadier H. J. Couchman, D.S.O., M.C., President of the National Institute of Sciences, presided.

Indian soils are known to be deficient in nitrogen. They are also generally deficient in organic matter. Together these deficiencies constitute one of the main problems of practical agriculture in India. But unmanured or poorly manured soils have continued to yield in many instances more or less the same average yield of crops. The recuperation, loss and supply of nitrogen has, therefore, attracted in recent years a good deal of attention from scientific workers in India. The problem of the disposal of molasses and bagasse confronts the sugar industry of India and their possible utilisation for increasing the productivity of the soil is also receiving considerable attention.

The papers numbering nineteen read at the Symposium by workers from different parts of India and Burma may be classified for convenience, though somewhat arbitrarily, under the following heads :—

- A. Recuperation and Loss of Nitrogen Contents of Indian Soils.
- B. Nitrogenous Manures.
- C. Analytical Methods.
- D. Nitrogen Status and Pedological Factors.

A

1. Prof. Dhar has in recent years raised a point of fundamental scientific and philosophic interest regarding the part played by *photo-synthesis* and *photo-catalysis* in the recuperation as also the loss of nitrogen in tropical soils. While not ignoring the part played by bacteria in these processes he emphasises that the current bacterial theory ignores altogether the possibilities of photo-chemical action. He and his collaborators have given data in several publications showing beyond doubt an increase in available and total soil nitrogen and crop yields following the application of material rich in carbohydrates, e.g., molasses. Cellulosic substances, cow-dung, sodium salts of higher fatty acids, etc., when mixed with soil also lead to nitrogen fixation. His basic ideas may be summarised as follows :—

The oxidation of carbohydrates can induce the photo-chemical fixation of nitrogen even in the absence of micro-organisms when suitable catalysts or photosensitisers are present. Thus it is stated that when a current of air is passed through a solution of carbohydrates, e.g., glucose or cane-sugar in presence of ferrous hydroxide, as much as 4 mgms. of nitrogen are fixed as ammonia per gram of glucose or cane-sugar oxidised. The efficiency is comparable to that obtained with cultures of *Azotobacter* thriving in flasks. It has been reported that the number of *Azotobacter* in the soil receiving sunlight is much less than in that kept in the dark, although the ammoniacal and total nitrogen contents of the former are greater than those of the latter. The humus and the moisture contents of the plots to which molasses has been added are greater than in the control plots. It is hardly necessary to mention that the accuracy of such experiments depends on the care taken in purifying the air. According to Dhar soil can also act as a photo-catalyst in this reaction and molasses can be substituted with good results for the carbohydrates in field experiments. Molasses also produces a residual effect on the soil nitrogen. Besides, potash, phosphate and lime contained in molasses render it a desirable fertiliser. The acids produced by oxidation, bacterial or photo-chemical, greatly ameliorate alkaline soils such as are met with in the United Provinces, Punjab and Mysore.

Dhar has investigated in detail the photo-oxidation of ammonia to nitrite and the part played by the decomposition of ammonium nitrite formed from ammonia and nitrite in the loss of nitrogen in the elementary gaseous form. Dhar and his collaborators also give an account of the rôle played by the photolysis of nitrate and recombination of nitrite with oxygen in the presence of light to form nitrate in the soil. This aspect is dealt with in a paper by Dr. Gopala Rao. Dhar further postulates that the C : N ratio has a significance different from what is usually ascribed to it. Mention has been made of the dependence of the fixation of nitrogen in soil on the energy obtained by the oxidation of organic matter by the various agencies at work, viz., bacteria, sunlight, inductors and catalysts. He suggests, moreover, that easily oxidisable carbonaceous materials such as carbohydrates hinder ammonification and nitrification and thus prevent, when present in excess, the loss of nitrogen from the resulting ammonium nitrite and promote the conservation of nitrogen in the soil. The general character of this retarding influence is emphasised and it is concluded that the C : N ratio in soils is not controlled by the energy requirements of the micro-organisms but is regulated by the ease with which the nitrogenous substances are oxidised by air in presence of other types of carbonaceous substances. These ideas form the basis of a correlated presentation of the work done at Allahabad in relation to the recuperation, loss and supply of nitrogen to the soil. Whatever differences of opinion may exist regarding some of the theoretical postulates and the conclusive nature of some of the experiments, there is no doubt that the work at Allahabad has given a great impetus to the scientific study of the nitrogen problem of soils.

In connection with the paper by N. R. Dhar, S. K. Mukherji, E. V. Sesha-charyulu, and S. P. Tandon [1] *:*

DISCUSSION

Professor V. Subrahmanyan (Bangalore) remarked that it was not clear whether micro-organisms were entirely excluded from the experiments with the catalysts and photosensitisers. In any case, micro-organisms are present and are active under soil conditions and the precise extent of their contribution (both by themselves and in presence of the catalysts or photosensitisers) is to be ascertained before concluding that they are inefficient. In Bangalore, an attempt was made by C. R. Harihara Iyer, R. Rajagopalan and the speaker to ascertain the relative contributions of micro-organisms and chemical oxidisers in bringing about soil oxidations and it was found that the micro-organisms were very much more active than the chemicals. It was also observed that microbial action was, to some extent, enhanced by the presence of chemical oxidisers such as manganese dioxide and ferric oxide.

There is no doubt that molasses assists in nitrogen fixation, but its contribution is not always so much as observed at Allahabad. At Bangalore it has been found to be very much less, the nitrogen fixed being equivalent to only 10–15 lbs. for every ton of molasses. Molasses is fairly rich in potash, but it is comparatively poor in phosphates. The observations regarding the production of organic acids are in agreement with the findings in Bangalore and elsewhere and it is probable that they are chiefly responsible for the reclamation of alkali land. Judging from the nature of the acids, it is very doubtful, however, if the reclamation will be permanent. There is a greater formation of acids under anaerobic than in aerobic conditions. Acid production in the soil is essentially a biological process and does not take place through direct oxidation as envisaged by Dhar *et al.* To be precise, there is both reduction and oxidation, the former yielding methane and the latter carbon dioxide and the acids. This is typical of most biological fermentations.

The data regarding the photo-oxidation on ammonia and ammonium salts would require checking. No figures are available regarding the actual quantities of ammonium nitrite produced in the soil from time to time. Moreover, it is not clear whether any attempt was made by the authors to collect and estimate the nitrates moving into substrata of the soil, especially after watering or rain as the case may be. The plots covered with zinc sheets would not have suffered from this disability and would naturally have contained more nitrate at the surface than the exposed ones. The possibility of volatilisation as ammonia is also to be reckoned with before considering losses and before enunciating any theory regarding the mechanism of the loss of nitrogen. The work of S. N. Gundu Rao at Bangalore would indeed suggest that at temperatures of 30° and above, nitrogen added as ammonium salts is, to a

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[1] No. 1 in the list of papers, see p. 72.

considerable extent, lost as ammonia. The theory regarding the loss of nitrogen from manure heaps (which is similar to the one which has been postulated by some previous workers) would also require modification. In this case, the evidence is very clear, as may be demonstrated by holding a piece of moistened red litmus for some time over a heap of decomposing manure.

The observations relating to available nitrogen of soils, as also the influence of temperature on the carbon-nitrogen ratio, have not been generally substantiated by other workers. This divergent observation is probably due to the nature of the technique adopted by the authors. Some standardisation in this direction will be highly useful.

Mr. T. J. Mirchandani (Bihar) said : He had been able to confirm some of the observations of Dr. Dhar. He observed that the pH of alkaline soil went down from 8·26 to normal when the soil was treated with 5% molasses. Regarding nitrogen, though in his experiments he noticed a fixation of 4–9 mgms. per 100 gm. of soil, the effect was temporary. There was a loss of nitrogen after 8 weeks of incubation.

Dr. Gopala Rao (Waltair) said : There was no doubt that the organic acids formed from the sugar in the molasses neutralised the alkali and helped to reclaim the alkaline soils but he doubted whether the reclamation could be permanent as the oxidation of the organic acids would leave behind the alkali.

2. Dr. Gopala Rao and Mr. Murty described some interesting experiments showing that when a glass vessel containing a solution of KNO_3 is exposed to sunlight there is no photolysis but in the presence of ignited ferric oxide photolysis takes place. Potassium nitrate in the presence of ferric oxide does not react in the dark. Sterilised soil also acts as a photo-catalyst in this reaction. Further, when ammonia in the form of ammonium chloride is added to a mixture of potassium nitrate and ferric oxide or red soil it is oxidised to nitrite. The rate of oxidation decreases as the pH increases.

In connection with the paper by G. Gopala Rao and K. S. Murty [1] *:*

DISCUSSION

Prof. V. Subrahmanyan (Bangalore) remarked that while it is true that nitrites are readily oxidised to nitrates in the soil, the reverse does not occur except in presence of abnormal quantities of fermentable organic matter. The nitrite content of the average soil is generally so small (often under two parts per million) that most workers of the present day do not make a separate estimation of that form of nitrogen. Furthermore, when considering the transformations of nitrite, the reaction of the medium has to be taken into

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consideration. Nitrite is highly unstable in acid media, moderately so under neutral conditions and quite stable in alkaline medium. While admitting the fundamental significance of the findings of Dr. Gopala Rao and his colleague, it is rather difficult to make out as to how they can be applied directly to the soil conditions.

Dr. G. Gopala Rao (Waltair) said (in reply to Prof. J. C. Ghosh): The reaction $NO_3' \rightarrow NO_2' + (O) - 81$ calories is endothermic, occurring with an absorption of energy of 81 cal. per gram molecule of nitrate reduced. This amount of energy corresponds to a quantum of radiation of wavelength 3500 Å. Experiments showed that there is very little reduction with light of wavelength greater than 3000 Å. But in the presence of ferric oxide or sterilised soil the reaction can occur in light transmitted by glass—the energy associated with a quantum of light in this region is much less than 81 cal.

He (the author) suggested that in the presence of a heterogeneous surface a part of the energy required is obtained from the reacting molecule adsorbed on the surface of the catalyst, the other part being supplied by a quantum of light of longer wavelength. It might be of interest to note that the critical energy increment of a reaction in the dark is much less in the presence of a heterogeneous catalyst than when it is occurring in a homogeneous medium.

3. Rao Bahadur Sahasrabuddhe summarised the work that has been done at Poona [1] with a view to explain the maintenance of fertility of soils of the arid and semi-arid tracts of the Bombay Deccan in the absence of manure with reference to the available nitrogen. He concludes that there must be considerable fixation of nitrogen from the atmosphere. The amount of nitrogen fixed increases with the moisture content. An optimum temperature is indicated. The fixation goes on even in darkness and no definite relation between the intensity of light and the fixation has been observed. Sugar has a beneficial effect provided that the proportion of the original organic matter is small and it has also a deleterious effect on the nitrifying power of the soil. Alkali salts are harmful but in one case they have been found to exert a stimulating effect. Field experiments confirm the laboratory results. Definite evidence has been obtained of the recuperation of nitrogen under field conditions in the dry farm tracts of the Bombay Deccan. The moisture added by the monsoon rains is beneficial. A peak in the nitrate and nitrite nitrogen content is observed about August. Organic and phosphatic manures have also a beneficial effect. The author has emphasised the necessity of correlating the nitrogen content with the concomitant factors, such as moisture and temperature. The results point to bacterial activity being the main factor in the recuperation of soil nitrogen.

4. In the absence of the author, Prof. V. Subrahmanyan read the paper on the Vicissitudes of Nitrogen in the Soil System by Rao Bahadur Viswa Nath.

There are periodical increases and decreases of nitrogen in manured as compared with similar unmanured plots in Coimbatore. The rate of nitrification and the accumulation of nitrates is greatest with ammonium sulphate, least with cattle manure and intermediate with green manure. While such results are expected it is pointed out that it is difficult to explain the loss of nitrogen which occurs chiefly in the end-product stage. There is no evidence of the movement of nitrogen into the deeper layers and of moisture saturation leading to denitrification. The nitrogen loss follows the peak value of nitrogen accumulation. Experiments with cane-sugar and sodium nitrate show that there are varying degrees of losses of nitrogen but there is little change with nitrate alone and the amount of loss increases as the C : N ratio is lowered. The loss of carbon is a function of the C : N ratio. In soil cultures containing sugar and no nitrate, the loss of carbon has been associated with the fixation of nitrogen from the atmosphere to maintain the ratio at about 10 : 1. In the experiments using sugar and nitrate in varying proportions there is a loss of nitrogen and the action of entirely different biological agencies is considered to be indicated. Denitrification is inadequate to account for the loss and photochemical decomposition can explain fixed losses but there must be some other factor.

In connection with the paper by B. Viswa Nath [1] :

DISCUSSION

After reading the paper, Prof. Subrahmanyan observed that it would not be fair to the author to discuss the paper in his absence. He wished, however, to point out that the Rao Bahadur's observations were generally in agreement with those of Dr. A. Sreenivasan and himself. Similar loss of nitrogen was also observed under water-logged soil conditions, the loss coinciding with the accumulation of ammonia in the medium prior to commencement of nitrification. As indicated in his comments on Prof. Dhar's paper, it would be useful to determine the extent of volatilisation of ammonia from the soil from time to time. Such a loss may be, at any rate, one of the unknown factors referred to by the Rao Bahadur. The concluding paragraph of the paper which is of the nature of a generalisation appears to have been based on results which were not given in the text.

Prof. N. R. Dhar (Allahabad) said : He was gratified that the author had accepted the explanation of nitrogen loss from soils under aerobic conditions as advanced by himself and collaborators (*Nature*, 1934, *134*, 572 ; *J. Indian Chem. Soc.*, 1935, *12*, 67, 756). He referred to the mechanism of the loss of

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[1] No. 4 in the list, see p. 72.

nitrogen in the gaseous form postulated by him and stated further that in acidic soils nitrous acid was formed which underwent decomposition and also increased the decomposition of ammonium nitrite. This explanation of nitrogen loss held good under all conditions when the soil was manured by any nitrogenous fertiliser.

The greater loss of nitrogen from soil manured with ammonium sulphate than with green and cattle manures were easily explained. In green and cattle manures carbonaceous substances retarded the processes of ammonification and nitrification and nitrogen loss. The increase of total nitrogen with green and cattle manures observed in several cases pointed to the fixation of atmospheric nitrogen and that his view points gave a satisfactory explanation. The observations of Sahasrabuddhe and Bal showing an increase of nitrogen under field conditions were clear from his results on the nitrogen fixation due to the oxidation of cellulosic materials. When comparative experiments were carried out, it was observed that the fixation in sunlight was greater than in the dark or diffused light.

5. Rao Saheb Bal gave an account of the fluctuation of organic nitrogen content of black cotton soils.[1] Considerable fluctuations and both loss and recuperation of nitrogen are observed in agreement with similar observations in the case of soils of the Punjab and of the Bombay Deccan. The organic nitrogen and the nitrogen fixing capacity both under field conditions and in pot cultures have been estimated. Recuperation of nitrogen is more frequent than the loss. There is no definite correlation of the fluctuations in the nitrogen content with the season but the nitrogen fixing power is somewhat higher in May, June and July. At the end of a period of nine years the pot culture experiments showed a definite increase in the nitrogen contents. Wheat has been cropped annually for nine years without any deterioration in organic nitrogen and a mixed crop of wheat and legumes does not show under the same conditions any significant increase in organic nitrogen over that in soils growing wheat alone.

6. The decomposition of sugars by *Azotobacter* and by mixed flora in soils in relation to the non-symbiotic nitrogen fixation was discussed by Prof. Subrahmanyan and Mr. Bhaskaran. The decomposition of sugar by even heavy inocula of *Azotobacter chroococcum* proceeds comparatively slowly. After the sugar is entirely used up, there is very little growth of the organism ; nor is there appreciable fixation of nitrogen. The residual organic matter is decomposed by the organism, but is not utilised in the fixation. In contrast to the above the mixed flora of the soil rapidly decomposes the

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sugar and though all of it disappears in the first four days there is very little fixation of nitrogen. From the 4th to the 12th day the organisms grow rapidly and fixation takes place. The organic acids formed during the first stage of decomposition are thus better utilised by the soil flora to fix nitrogen than sugar. It has been stated that the mixed calcium salts of organic acids formed during the aerobic decomposition of carbohydrates can be utilised in the fixation of nitrogen. These products are decomposed comparatively slowly, but the return of nitrogen fixed for the carbon utilised (under 1 : 20) is more than three times that obtained when a carbohydrate is applied directly to the soil.

The efficiency of fixation by the mixed calcium salts under different conditions has been studied. It has been found that the maximum fixation takes place when the concentrate is applied in quantities corresponding to about two tons of organic carbon per acre. The nitrogen fixed by this will be about 2 cwts. and would correspond to 13·5 cwts. of protein, which, in turn, would be equivalent to 2·5 tons of a good seed cake. The presence of sugar or other fermentable materials does not appreciably interfere with the fixation by the calcium salts.

In connection with the paper by T. R. Bhaskaran and V. Subrahmanyan [1]:

DISCUSSION

Prof. N. R. Dhar (Allahabad) said (also referring to the paper by A. Sreenivasan and V. Subrahmanyan): Löhnis and Pillai (*Centrbl. Bakt.*, 1908, 11, *20*, 781) reported that the nitrogen fixed per gram of energy material varied from 4·36 to 9·96 mgms. with different sugars, whilst with calcium butyrate, potassium oxalate, sodium citrate, etc. it varied from 0·16 to 0·96 mgm. Hence the results recorded by the authors were very different from those existing in the literature and needed further confirmation. Because nitrogen fixation was an endothermal reaction, the amount of fixation must depend on the energy available. It is well known that 676 calories are available in the oxidation of a gram mole of glucose whilst 376 calories are obtained from the oxidation of one gram mole of propionic acid. Hence from the energy point of view less fixation was to be expected from propionic acid as an energy material than with glucose. The results of his own experiments showed that when soil was mixed with sodium acetate, sodium oxalate, sodium tartrate, etc., very little nitrogen fixation took place under aerobic conditions, whilst with sodium salts of oleic acid, palmitic acid and stearic acid, glucose, cane-sugar, starch, mannitol, etc., large amounts of nitrogen fixation was observed. Moreover, carbohydrates when added to soil under normal conditions could be detected even after several months.

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[1] No. 6 in the list, see p. 72.

He also referred to the nitrogen loss arising out of the decomposition of ammonium nitrite and nitrous acid. He mentioned that Sir John Russell, J. G. Lipman and others had frequently stated that the loss of nitrogen from soils was mostly due to the escape of gaseous nitrogen and suggested that the problem might be studied from this point of view.

Mr. T. J. Mirchandani (Bihar) said: In one of the tables an increase of nitrogen from 1·25 to 1·67 was to be found in 4 to 12 days in the test solution, whereas in the control (unsterilised soil) there was greater increase, viz., from 2·10 to 2·77. Again in the presence of calcium salts the Bangalore soil fixed 0·32 mgms. of N as against 0·50 mgms. in the Kalar soil of Sind. He wondered whether this difference was due to high alkalinity or the authors had some other explanation to offer.

He remarked that these researches, if confirmed, would give a new orientation to our concept of nitrogen fixation but a lot more data was required before it could be accepted.

Mr. T. R. Bhaskaran (in reply) stated that his work was of a different type from those referred to by Prof. Dhar. Very little systematic work has so far been carried out with the mixed flora of the soil. A large amount of work has been conducted with pure strains of *Azotobacter*, but, as may be seen from the present study, such enquiries cannot throw much light on the mechanism of fixation in the soil. As for the energy relations of fixation, very little accurate information is still available. It may be stated, however, that it has no direct relation to the calorific values of the materials concerned. A large part of the applied material is utilised by the fixing organisms to form side products, so that it is not correct to argue on a purely energy basis. Furthermore, no attempt has been made in the present study to correlate the fixation with the utilisation of any one of the volatile fatty acids. Indeed, the material employed was a mixture of calcium salts together with other minerals (originally present in solution) such as iron and aluminium which are precipitated by lime.

In reply to Mr. Mirchandani, he stated that experimental material contained only the soluble products of fermentation, whereas the control observations related to the original sugars. The product resulting from the latter included the nitrogen of the sediment as also the small quantities of nitrogen fixed by the sugar during the first four days—hence the difference. The object of the experiment was primarily to show that the supernatant liquid was responsible for the major part of the fixation. In reply to the second question, he stated that the difference was not after all very considerable and was made up by the 17th day when it was 0·91 mgms. in the *Kalar* soil and 0·93 mgms. in the Bangalore soil. It is not improbable, however, that the alkalinity of the *Kalar* soil was favourable to the fixation in the early stages.

Prof. V. Subrahmanyan drew attention to the practical significance of the findings. He pointed out that if materials like molasses which are so inconvenient to handle can be subjected to a preliminary anaerobic fermenta-

tion, the resulting product can, after neutralisation, be concentrated to a dry powder which is a more potent nitrogen fixating agent than the original material. It can be stored in bags and will stand transport from one centre to another. It has already been tried out on an experimental basis in Bangalore with highly satisfactory results.

7. Mr. K. M. Pandalai discussed the mechanism of nitrification in soil. When cultured in artificial media, the nitrifying organisms, *Nitrosomonas* and *Azotobacter*, are paralysed even by minute quantities of organic matter. On the other hand, nitrification in nature—particularly in soil and sewage—proceeds in presence of large quantities of organic matter. This incompatibility of behaviour of the classical nitrifying organisms in pure artificial cultures with that in their natural environments may be explained as being due to one or more of the following.—(1) The nitrifying bacteria function in association with the saphrophytes of the soil. (2) There are in soil several strains of organisms other than the classical nitrifiers which could tolerate fairly large quantities of organic matter and nitrify ammonia. (3) All nitrifiers are heterotrophic at some stage of their lives.

In connection with the paper by K. M. Pandalai [1]:

DISCUSSION

Prof. N. R. Dhar (Allahabad) said : He would draw the attention of the author to the work of Fuller and Rettger (*Soil Sci.*, 1931, *31*, 217) in which it had been stated that *Azotobacter* could fix atmospheric nitrogen even in the presence of different ammonium salts. It seemed that the greater nitrification observed with a mixture of *Azotobacter* and *Nitrosomonas* was due to the greater amounts of ammonium salts present in the system caused by nitrogen fixation which is effected by *Azotobacter* fed by glucose.

Mr. K. M. Pandalai (Bangalore) stated : The ammonium compounds in nitrogen fixing cultures of course increased the growth of the *Azotobacter*, but in a majority of the cultures there was slight depression of nitrogen fixation. Fuller and Rettger write ' the simple inorganic compounds seem to be utilised easily by *Azotobacter* with the result that growth is increased and nitrogen fixation either relatively or actually depressed '.

The question of the formation of ammonia or its salts by the activity of the *Azotobacter* in nitrogen fixing cultures was still unsettled (Compare Burk, *Soil Sci.*, 1936, *41*, 81). He said that the increase in the concentrations of ammonium salts by *Azotobacter* activity, if it occurs at all, was negligible.

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[1] No. 7 in the list, see p. 72.

Fuller and Rettger also found that in presence of peptone, while there was more growth of *Azotobacter*, there was depressed nitrogen fixation. These were incompatible and the mechanism of the enhanced nitrification should be explained as due to entirely different causes. Further, the explanation the author offered also applied to *B. mycoides* in presence of which there was also enhanced nitrification.

8. Mr. Mirchandani pointed out the beneficial effects of combining organic manures with artificials. He has observed that there is a definite improvement (about 4–9 mgms. per 100 gms. soil in 2 months) in the total nitrogen content of the soil when incubated with molasses. He suggests that molasses should be incorporated in the soil 4–8 weeks before putting the land to crop. The addition of molasses increases the nitrogen content by 4–9 mgms. of nitrogen per 100 gms. of soil in two months. Composts obtained from sugar-cane trash have been found to be very suitable for wheat and maize.

In connection with the paper by T. J. Mirchandani [1]:

DISCUSSION

Prof. N. R. Dhar (Allahabad) said : He was glad that Mr. Mirchandani had been able to confirm the results of Dhar and his collaborators that, on the addition of molasses to soils in Bihar, atmospheric nitrogen was fixed. He (Mirchandani) himself had been able to obtain, using a large amount of molasses, a fixation of 180 lbs. of nitrogen per acre of soil, whilst Dhar and Mukherjee obtained 112 lbs. of nitrogen fixed on applying 3 tons of molasses per acre. The soil with which he experimented contained a higher percentage of total nitrogen (0·06%) than that used by Dhar and Mukherji (0·045%). Mr. Mirchandani obtained less fixation than that recorded by Dhar and co-workers, when the amounts of molasses used were identical. It is well known that the greater the nitrogen content of the soil, the less is the fixation.

He was also glad to find that *Usar* and alkaline soils had been successfully reclaimed by the application of molasses. If the experiments of Mr. Mirchandani were continued, he (Dhar) believed that the observations of Dhar and his co-workers, namely that the nitrogen fixed by the application of carbonaceous substances to the soil was retained for a much longer period than when ammonium sulphate was used, would be confirmed. There was certainly a residual effect of molasses and other carbonaceous materials but not in the case of ammonium sulphate.

Prof. V. Subrahmanyan (Bangalore) enquired as to how in some of the experiments, farmyard manure gave lower yields than the controls. There

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[1] No. 8 in the list, see p. 72.

was also heavy loss of nitrogen from some of the control series. Was there any explanation for this ? He suggested that in addition to nitrates, we should take into consideration the release of amides and amino-acids which could be directly assimilated by plants.

Mr. T. J. Mirchandani (Bihar) said : (Replying to Prof. Dhar.) He was unable to agree with Dr. Dhar that the green manuring would ultimately make the soil more alkaline. In fact the immediate effect of decomposing green manure was to make the medium slightly acidic but in the long run the acidity disappeared.

(Replying to Dr. Subrahmanyan.) If one looked at the table more critically it was found that the habitation manure had definitely given a higher yield of grain as well as of straw in both the crops. That was really the main point in the table. Regarding the use of amino-acids by plants he maintained that the evidence was not conclusive though it was slowly accumulating.

9. Mr. P. K. De discussed the question of fixation of nitrogen in rice soils.[1] Under water-logged conditions nitrogen is definitely fixed in rice soils and the amount increases with the pH. Algæ are considered to be responsible for the fixation. These are important observations but it is not yet known whether the algæ themselves are capable of fixing the nitrogen or whether they do so in symbiosis with other organisms. Under dry conditions fixation is much smaller and is not so general as under water-logged conditions. Nitrogen fixing organisms different from *Azotobacter*, but probably belonging to the same genus, have been found to fix nitrogen and have been isolated pure. They have a slow growth in nitrogen-free mannite medium and are characterised by copious slime formation, non-motility and non-pigmentation. Rice plants do not thrive in sterilised sand using sterilised seeds and there is no fixation of nitrogen. Nitrogen fixing organisms are present in rice leaves. Regarding the loss of nitrogen from water-logged soils decomposition of ammonium nitrite is not responsible for it. The supply of oxygen being limited the ammonia is first oxidised to hydroxylamine and then to gaseous nitrogen and water.

In connection with the paper by P. K. De :

DISCUSSION

Prof. V. Subrahmanyan (Bangalore) observed : While it was possible that there was some fixation of atmospheric nitrogen in rice soils, the nitrogen thus added could not entirely account for the maintenance of the fertility. The fertility of Bengal and indeed of the whole of the Indo-Gangetic plain is largely traceable to the fine silt deposited by the rivers. Fresh river silt

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[1] No. 9 in the list, see p. 72.

is generally rich in nitrogen, some samples containing over 2,000 parts per million. In South India, with the construction of two huge dams in the upper reaches of the Cauvery, the natural fertility of the Deltaic regions had appreciably diminished in recent years.

He enquired whether any quantitative estimation of the hydroxylamine formed or of the elementary nitrogen was carried out. His studies with substances of varying C : N ratios showed that the loss of nitrogen from the water-logged soil could be largely accounted for by volatilisation of ammonia.

B

10. Prof. Subrahmanyan discussed sewage as a source of nitrogen supply. It is one of the most economical methods of supplying nitrogen and other fertilising ingredients to the soil. Its application to land is attended, however, by various problems—chemical as well as biological—the elucidation of which is of the greatest importance both to agriculture and public health.

Continuous application of raw sewage or effluent (after one of the various treatments) leads to soil sickness. The land becomes smelly and the crops fail. The changes attendant on sewage sickness have been discussed. Methods of reclaiming sick soils are indicated.

In connection with the paper by V. Subrahmanyan [1]:

DISCUSSION

Prof. N. R. Dhar (Allahabad) said : Experience at Allahabad had been different because in the Naini Agricultural farms all crops were grown with ordinary sewage water without purification or dilution all the year round. The foods cooked from these crops were as healthy as from normal materials. The large cattle population of the farms thrived very well on the grass grown with undiluted or unpurified sewage water. Under the influence of the tropical sun and high temperatures prevailing in India, the carbonaceous and nitrogenous organic substances present in sewage are readily oxidised when mixed with the soil yielding useful products necessary for plant growth. The problem in this country was to save the carbon and nitrogen from too quick oxidation and in the alluvial soils of northern India the sewage water without purification or dilution, when properly mixed with the soil, readily added ammonium salts, nitrate, phosphates, potash, etc., for the growth of plants. The soil sickness observed in colder countries on the application of sewage was chiefly due to the deficiency of oxidation of the nitrogenous and carbonaceous compounds and to the presence of soaps.

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[1] No. 10 in the list, see p. 72.

Mr. T. J. Mirchandani (Bihar) inquired what would be the residual value of the addition of such large quantities of sewage to the soil because all the nitrogen could not possibly be utilised by the crops.

The interaction of nitrogen and P_2O_5 was now well established in that such combination resulted in better crop yields. It was necessary, therefore, to have an idea of the phosphoric acid content of the sewage and sludge that was applied and then to see the interactions with and without extra phosphoric acid. He also inquired if any explanation could be offered by the author of the low yield of potatoes obtained by him when he treated the soil with super alone. The yield was found to be a little over half that of the control. Regarding quality of crops he (Mr. Mirchandani) was in a position to confirm by his own observations that in sugar-cane a high dose of nitrogen tended to decrease its sugar content. All easily nitrifying fertilisers would have the same effect.

He remarked that it would have been very useful if in the case of sewage experiments on elephant grass and lucerne the application of the sewage had been for a limited period only and not throughout the life of the plant and the results watched.

Dr. A. T. Sen (Dacca) said : Prof. Subrahmanyan observed a failure of grain in crops fed on effluent rich in available nitrogen. His experience with rice was that if nitrogen absorbed by this plant be such that the percentage of nitrogen in the straw at harvest exceeded 0·7, little or no grain production took place. Was the percentage of nitrogen estimated in the crops which he had tried when the grain failed ? A knowledge of the limiting nitrogen content for grain production of most of the Indian grain crops was of obvious importance in practical agriculture.

Prov. V. Subrahmanyan (in reply) stated that the Naini Farm might be an exception, but his observations were nevertheless true of most sewage farms in the world. Continued application of undiluted sewage would lead to soil sickness under all climatic conditions. He had no opportunity to examine the products of the Naini Sewage Farm, but had no doubt that they would compare unfavourably (in general quality) with those raised on water in the same locality.

Replying to Mr. Mirchandani, he stated that both the raw sewage and sewage sludge had residual values, but diluted sewage effluent has practically none. The bulk of the phosphorus of sewage passes into the sludge, so, if only the effluent is used, it has to be supplemented by a phosphate fertiliser. Sewage sludge contains two to three per cent of phosphoric acid (P_2O_5), a large part of which is available to the plant. It is difficult to explain why potato gave a reduced yield on application of super alone. The soil was deficient in nitrogen and it is probable that the phosphate-stimulated roots suffered more than the untreated ones. The experiments with elephant grass and lucerne were carried out over a long period so as to stimulate the usual grass-forming practice. Moreover, the extended experiments would

show whether there was no falling off in yield or any abnormality observable consequent on continued application of sewage.

He agreed with Dr. Sen that it would be useful to have an idea of the limiting concentration of nitrogen but in case of heavy applications of sewage, the issues were complicated by soil sickness, plant disease, insect pests and such like.

11. Messrs. Pal and Rakshit discussed the most suitable time of application of oil cakes to the field for quick-growing crops.[1] Three different kinds of oil cakes have been used. The formation of nitrate consequent on the decomposition of the cakes has been followed. The addition of the cake at first causes a small retardation in the nitrification. This, however, lasts only for a short interval. Lime quickens the decomposition and also intensifies the nitrification. The application of the cake during the *Rabi* season is recommended and is considered to be more beneficial than its application in the *Kharif* season. This is the present practice in some parts of Bengal for growing potato. The succeeding crop, usually jute, can fully utilise the unspent and freshly formed nitrate.

12. Prof. Subrahmanyan and Dr. Sreenivasan discussed the transformation of organic nitrogenous material in swamp soils.[2] A large part is converted into ammonia. The conversion into ammonia and its loss increases with the $C:N$ ratio and the amount of added material. Volatilisation of ammonia favoured by the high temperature is considered to be responsible for this loss. Addition of carbonaceous material in quantities which would raise the $C:N$ ratio to $15:1$ has been found to be effective in reducing the loss of nitrogen.

13. Dr. Sen discussed the nitrogen requirements of the rice plant in different stages of its growth. Analysis of the plant shows that absorption of nitrogen continues till harvest. The percentage of nitrogen in the plant increases during the first six weeks after transplantation and then decreases. Pot culture experiments show that if the nitrogen supply is cut off at any stage the growth is checked but even the four-week old seedling survives and bears grain. On using excess of nitrogen failure of grain has been observed. The presence of boron in the culture medium improves grain formation and causes an increase in the dry weight of the plant. The maximum loss of nitrogen from the culture solution takes place during the seedling and ripening stages. The results indicate the desirability of increasing the available nitrogen status

of the soil during the active vegetative stage and the beginning of the flowering stage. The application of niciphos to paddy soil in conjunction with treatments with various combinations of lime, potash and magnesia show a statistically significant though not very marked increase in the grain yield as compared with controls.

In connection with the paper by A. T. Sen [1]:

DISCUSSION

Prof. V. Subrahmanyan (Bangalore) stated: It was difficult to understand the nitrogen loss from culture solutions. He wanted to know whether the distribution was completely worked out and the balance determined. In addition to possible loss in the elemental form, volatilisation of ammonia may also be considered.

Mr. T. J. Mirchandani (Bihar) said: The nitrogen content of the rice plant at transplanting appeared to be rather low. Was it possible that if transplanting was delayed, the result was that with the increase in dry weight the dilution effect on nitrogen was noticed? The author's contention that rice took up nitrogen till harvest required confirmation. It would be useful to have tiller counts so as to correlate that function with nitrogen uptake. If the nitrogen was cut off at a certain stage of plant growth there would be a translocation of nitrogen from some tillers to the surviving ones.

Regarding the non-formation of grain when the nitrogen was supplied in excess so as to give 1·2 per cent nitrogen in straw, such conditions were not likely to occur in general practice. The observations of the author, however, had importance in so far as they gave a warning against the excessive use of nitrogen for the rice crops.

Prof. N. R. Dhar (Allahabad) said: In the rice fields of Bengal in the dry season the straw, plant residues, etc., present in the soil are oxidised with the liberation of energy required for nitrogen fixation. In the wet periods, the oxygen dissolved in the water and the oxygen adsorbed on the soil surface helped the oxidation and decomposition of the cellulosic materials and this leads to nitrogen fixation in the soil. This addition of nitrogen to the soil stopped soil exhaustion and maintained a fairly steady yield of crops year in and year out under tropical conditions although the soil is not manured by artificials.

Dr. A. T. Sen (Dacca) said: (In reply to Prof. Subrahmanyan.) Under water-logged conditions nitrogen would be lost from the soil in the elemental

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form according to the equations developed by his colleague Mr. P. K. De and given in his paper. The reaction would proceed according to equation (2) in a normal aerated soil. Under submerged conditions oxygen supply becomes limited and the reaction proceeds according to equation (3). The soils used by them (Sen and De) being acid (pH—5·0) there was little possibility of nitrogen being lost as ammonia.

(In reply to Mr. Mirchandani.) He agreed that 1·25 per cent nitrogen in the rice straw at harvest could not be realised in the field. It was the percentage obtained in the water culture but, as stated before, little or no grain production took place if the percentage of nitrogen in rice straw at harvest exceeded 0·7. The low percentage of nitrogen of the rice plants at trans-plantation was obviously due to the fact that he (Sen) did not manure the seed beds as heavily as Mr. Mirchandani or others did. It would be wrong to say that manuring of the seed bed alone was the last thing to do in rice cultivation. Large increases in yield were obtained in Japan, Italy and elsewhere by top dressings of nitrogenous fertilisers following transplantation. On the contrary his (Sen's) results indicated the possibility of considerable loss of added nitrogen if seed beds were manured heavily. As regards the tillering of paddy he agreed with Prof. Agharkar that it was mainly controlled by the oxygen supply to the roots. If the oxygen supply was large, as in semi-moist soils, tillering would be limited; if the supply was small, due to excessive submergence, the tillering would again be limited. But it would be wrong to say that the golden mean was 6 inches of submergence. The optimum submergence might vary from a few inches to several feet depend-ing on the variety of the paddy chosen.

Dr. H. Chaudhuri (Lahore) said : The failure of nitrogen fixation in the soil with the increase of acidity mentioned by Dr. Sen was due no doubt to the failure of the nitrogen fixing organisms to grow in acid media. In all rice fields in E. Bengal green organisms grew abundantly and it had been shown that the nitrogen content of the soil increased under those conditions. Some two years back samples of soil and water from the rice fields in Faridpore were sent to the speaker by Sir Bryce C. Burt (then Mr. B. C. Burt) for analysis. The soils were put in different sterile flasks containing distilled water, and during six months following the green organisms appearing in the culture flasks isolated. These consisted mostly of blue green algæ and only a few green algæ. When examined under the microscope after proper staining, the mu-cilage coatings of the blue-green algæ were found to be full of bacteria. Next the bacteria were plated and by growing in nitrogen free media it was found that they fixed atmospheric nitrogen. When these were grown in media of different pH values, it was found that more nitrogen was fixed on media having pH value 7·0 or over. The organisms ceased to grow in definitely acid media and so no nitrogen fixation could take place. The algæ without the bacteria had no power of fixing nitrogen nor had the rice unaided any power of fixing nitrogen.

14.   Mr. H. N. Pal described his experiments conducted at Jorhat in Upper Assam on the manurial treatment of sugar-cane soils.[1] The average nitrogen content of the (top) soil is 0·09 per cent.   Sugar-cane grown on this soil shows signs of nitrogen starvation and gives a poor yield.   A rotation of crops and the application of cow-dung and oil-cake give satisfactory results.   The application of about 300 mds. of cow-dung along with 1000 lbs. of oil-cake has been observed to produce the best yield.

C

15.   Prof. Subrahmanyan and Dr. Sreenivasan discussed the errors of analytical methods of sampling and the errors arising out of soil heterogeneity in relation to the observed fluctuations of nitrogen contents of soils.[2]   They have compared the dry and wet methods of digestion and have observed a difference of as much as 25 per cent in some soils.   The official dry method gives low and discordant values.   The distribution of nitrogen in finely ground samples within each plot shows great variations from time to time which might be mistaken as periodic fluctuations.   It is suggested that the movement of soil albuminoids as a result of a partial peptisation by the dilute salt solutions in the soil should also be taken into account.

16.   Mr. K. M. Pandalai proposed methods for determining nitrous and nitric nitrogen in solutions.   The inaccurate results (generally low) invariably obtained for the nitrous nitrogen content of soils were stated to be due to (1) the extreme instability of that form of nitrogen and (2) the inevitable presence of organic matter in soil extracts.

The addition of a fair excess of slaked lime suspension clarified the extract and at once stabilised the nitrous nitrogen.   A further addition of small quantities of copper sulphate and lead acetate solutions rendered the extract protein-free, sugar-free and entirely colourless and facilitated filtration.

The method described in the paper took only 1 to 1½ hours and yielded very satisfactory results with a variety of tropical soils, and the author recommended it for the study of nitrogen changes in soil.

In connection with the paper by K. M. Pandalai[3] *:*

DISCUSSION

Dr. G. Gopala Rao (Waltair) said: It was necessary to study whether the oxidation of nitrite to nitrate by hydrogen peroxide in acid solution

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was complete. His results showed that it was not complete and he suggested that the conditions of quantitative reaction should be studied in alkaline solution.

When the unused hydrogen peroxide was back titrated against standard permanganate it should be borne in mind that the permanganate would interact with any unoxidised nitrite as well. It was well known that permanganate could oxidise nitrous acid.

Mr. K. M. Pandalai (Bangalore) said : (in reply to Prof. J. N. Mukherjee) control experiments with the reagents were done.

(In reply to Mr. Mirchandani.) A mixture of acid and salt could not be used. The whole question of oxidation of $HNO_2 \rightarrow HNO_3$ was one of pH so that if nitrite was to be stabilised an alkaline medium would have to be used.

(In reply to Dr. G. G. Rao.) A large excess of H_2SO_4 (1 : 1) should be used ; the oxidation was instantaneous and the stoichiometric quantity of nitrate was obtained.

17. Mr. R. Rajagopalan in presenting the paper by himself, Mr. C. R. Harihara Iyer and Prof. V. Subrahmanyan [1] said : The procedure consisted in treating the material to be digested with a small quantity of mercuric oxide and sufficient excess of 2 : 1 sulphuric acid. The mixture is then raised to boil and treated with either solid dichromate or an aqueous solution of chromic acid. The boiling was continued for 30 minutes after which the digest was cooled and reduced with excess of alkali sulphite followed by zinc. The product was distilled in the usual way.

D

18. Dr. S. P. Aiyar gave a systematic account of the nitrogen status of the soils of Burma in relation to various pedological factors. [2] Burma soils have been classified into five groups on the basis of rainfall and altitude. The percentages of carbon and nitrogen, and the pH, rainfall and the soil texture expressed as the sum of the percentages of clay and silt fractions for each of the groups have been tabulated. The following conclusions have been arrived at : (a) In agreement with Jenny's law the mean nitrogen content has been observed to increase with the rainfall ; the nitrogen content also increases with fall in temperature ; large differences in rainfall are counterbalanced by small differences in temperature ; (b) water-logging increases the soil organic matter ; (c) the organic matter content also depends on the covering vegetation and cultivation ; (d) no definite relation seems to exist between the nitrogen content and the texture of the soil but it is pointed out that the method of expressing the texture is liable to give wrong results. Manurial experiments on paddy crops in pots and

in the field show that nitrogen when added as ammonium sulphate always induces a good response. Nitrates, ammonium bicarbonate, urea and calcium cyanamide are less effective. Phosphate when used in combination with ammonium sulphate very often produces better results than with ammonium sulphate alone. Potassium sulphate produces no response. Green manure and other organics which liberate ammonia show marked increase of the yield. In tropical paddy growing areas there seems to exist a limit beyond which the yield cannot be increased, whatever be the treatment. Experiments with sugar-cane show that ammonium sulphate is more effective than nitrate, and potash or phosphate appears to be unnecessary. It is to be hoped that further systematic work on similar lines will be carried out in other parts of the country.

19.   Messrs. Wad and Aurangabadkar gave an account of the carbon and nitrogen contents of typical soils of Bundelkhand, Malwa and Rajputana. These quantities have been estimated at different depths of the soil profile and their relation to temperature, rainfall, moisture holding capacity, productivity and mechanical composition have been discussed. The carbon and nitrogen contents of these soils are usually low compared to those in temperate regions. The C : N ratio seldom exceeds 10 : 1. No relation has been found to exist between the C : N ratio and the temperature, humidity and the moisture holding capacity. Lysimeter experiments with profiles of different soils show that the yield of cotton is not related to the nitrogen content. The application of nitrogenous manure does not always produce a response in the crop yield. Nitrogen content of the surface horizon of virgin soil is lowered by cultivation and the lowering appears to be inversely proportional to the content of the sand free fraction. The behaviour of the second horizon seems to differ from that of the first and sometimes works in an opposite direction. It is considered that differences in productivity depend chiefly on the extent to which the supply of nitrogen and moisture is similarly maintained by the first two horizons of the soil.

In connection with the paper by Y. D. Wad and R. K. Aurangabadkar [1] *:*

DISCUSSION

Prof. V. Subrahmanyan (Bangalore) wanted to know if the authors had got data to prove their statement that the C : N ratio varies with temperature.

Mr. R. K. Aurangabadkar, in reply, said : They had not made a statement to that effect. On the other hand they found no correlation between the carbon or nitrogen contents or their ratios in the different soils and the climatic factors like temperature, humidity or rainfall.

Prof. N. R. Dhar (Allahabad) said : The observations in this paper became clear if the authors would take into consideration the fact first emphasised by Dhar and Mukherjee (*J. Indian Chem. Soc.*, 1936, *13*, 233) that the percentage of *available* nitrogen in tropical soils is much greater than in the soils of temperate climates. As the soils used by the authors contained a fairly large proportion of available nitrogen, it was not expected that a favourable response to nitrogen manuring would be observed and this had been actually reported by the authors. Dhar and Mukherjee (*J. Indian Chem. Soc.*, 1934, *11*, 883; 1935, *12*, 436), from the analysis of well-aerated soils from different parts of India and other countries, had shown that the C : N ratio of soils was greater the warmer the country. This is in agreement with the observation of McLean (*Journ. Agric. Sci.*, 1930, *20*, 348). Jenny (*Soil Sci.*, 1929, *27*, 168) reported contrary results because his conclusion was based on extrapolations. If the authors carried on experiments with well-ploughed soils they were likely to obtain C : N ratios of their soils larger than 9 or 10.

Mr. R. K. Aurangabadkar, in reply, said : A higher percentage of available nitrogen may not necessarily result in the supply of greater quantities of nitrogen to plants. Because the total available quantity depends upon both the total content of nitrogen and its availability. It is equally essential that the superior availability of nitrogen should not be short-lived, but persist sufficiently long. This may not happen in many tropical soils, as shown by the results of nitrification tests carried out at Indore.

NITRIFICATION IN UNMANURED SOILS, MONSOON CONDITIONS, INDORE, 1933.

Mgms. of nitric N per 100 gms. of oven-dry soil.

Surface soil.	Interval in days from start.						
	0	21	42	63	84	105	126
Black cotton, Indore ..	0·17	1·08	1·93	2·32	1·98	1·03	0·82
Sandy loam, Jaipur ..	0·12	..	1·32	..	..	0·52	0·53

The percentages of carbon and nitrogen in soils and consequently their ratios indicate the kind of residue left in them as a result of the various types of decay of organic material possible in the prevailing environment. The nature of the decomposition is determined by the combined influence of the prevailing temperatures, moisture and oxygen contents and the chemical nature of the substances taking part in the processes. Hence, it is natural that the C : N ratio is not determined solely by a single factor. An apparent dominance of one factor may be found on an examination of soils, otherwise similar, but exposed to variations in its intensity, larger than those of the others.

Inferences based on such observations may not be universally applicable. This is shown in this paper by the carbon and nitrogen contents and their ratios found in soils—both virgin and cultivated—formed under widely different conditions and in regions with prevailing temperatures equally varying. The influence of temperature is modified by that of differences in the moisture and air regimes as well as the chemical and physical nature of the clay complex.

LIST OF PAPERS

Group A. *Recuperation and Loss of Nitrogen Contents of Indian soils.*

(1) Nitrogen transformations in the soil.   By N. R. Dhar, S. K. Mukherji, E. V. Seshacharyulu, and S. P. Tandon.

(2) Photocatalytic reduction of nitrate and simultaneous oxidation of ammonia to nitrite.   By G. Gopala Rao and K. S. Murty.

(3) Fluctuations, recuperation and fixation of nitrogen in the soils of Western India.   By D. L. Sahasrabuddhe.

(4) The vicissitudes of nitrogen in the soil system.   By B. Viswa Nath.

(5) A study of the fluctuations in organic nitrogen content of black cotton soil under varying conditions of cropping.   By D. V. Bal.

(6) Some new aspects of the mechanism of nitrogen fixation in the soil. By T. R. Bhaskaran and V. Subrahmanyan.

(7) A new aspect of the mechanism of nitrification in soil.   By K. M. Pandalai.

(8) Nitrogen status of Indian soil.   By T. J. Mirchandani.

(9) A note on the nitrogen supply of rice soils.   By P. K. De.

Group B.   *Nitrogenous Manures.*

(10) Sewage as a source of nitrogen supply to the soil.   By V. Subrahmanyan.

(11) Decomposition of oil-cakes and formation of nitrite.   By G. B. Pal and S. C. Rakshit.

(12) Transformations of nitrogen in the swamp soil.   By A. Sreenivasan and V. Subrahmanyan.

(13) Some field and water culture experiments with rice.   By A. T. Sen.

(14) Manurial treatments for remedying the nitrogen deficiency of soils of Upper Assam for growing plant canes.   By H. N. Pal.

Group C.   *Analytical Methods.*

(15) Some factors influencing studies on nitrogen fluctuations in soil plots. By A. Sreenivasan and V. Subrahmanyan.

(16) Determination of nitrous and nitric nitrogen in soils.   By K. M. Pandalai.

(17) An improved method of estimating nitrogen in soils and plant materials.   By C. R. H. Iyer, R. Rajagopalan, and V. Subrahmanyan.

Group D.   *Nitrogen Status and Pedological Factors.*

(18) The nitrogen status of the soils of Burma.   By S. P. Aiyar.

(19) Nitrogen and carbon status in relation to soil productivity.   By Y. D. Wad and R. K. Aurangabadkar.

NITROGEN TRANSFORMATIONS IN THE SOIL.

By N. R. Dhar, S. K. Mukerji, E. V. Seshacharyulu, *and*
S. P. Tandon, *Allahabad University.*

(Read at Symposium, August 29-30, 1936.)

Introduction.

Although manures from farmyards and night-soil are in use in agriculture all over the world from ancient times, the exact nitrogen requirement of plants was not worked out till 1855, when Lawes and Gilbert published their classical reports at Rothamsted. Even the great chemist, Liebig did not realise the importance of supplying nitrogenous manure to the soil as is evidenced from the following lines from his ' Chemistry in its Application to Agriculture and Physiology ' (1840) and his article in Farmer's Magazine 1847, *16*, 511 :—

' If the soil be suitable, if it contain a sufficient quantity of alkalis, phosphates and sulphates, nothing will be wanting. The plants will derive their ammonia from the atmosphere as they do carbonic acid.'

In India the problem of the supply of nitrogenous manure to the soil is of greater importance than in Europe because the nitrogen content of Indian soils is generally half of that present in European soils. Dr. J. A. Voelcker in his report on the ' Improvement of Indian Agriculture ' (1893) stated as follows :—

' On looking into analysis of Indian soils which have been recorded and others which I have made myself, I find that, with possible exception of black cotton soil, Indian soils are generally very deficient both in organic matter and in nitrogen.'

The Royal Commission on Agriculture in India (1928) also reported that Indian soils are mainly deficient in combined nitrogen and the manurial problem in this country is chiefly that of nitrogen deficiency. The uncombined nitrogen present in the air is not directly absorbed by the majority of the plants and cannot serve as a plant food material.

In European and more advanced countries of the world, ammonium salts, urea, nitrates, cyanamide, etc. are manufactured and are supplied to the soil as manure for the nitrogen need of plants and improving the crop yield. Urea, cyanamide, etc. form ammonium salts in the soil. The advanced nations are competing with each other in the manufacture of ammonium salts and nitric acid by the combination of the Haber-Bosch and Ostwald processes. The addition of ammonium salts to the soil largely improves the yield of crops

and under favourable conditions the yield can be doubled, e.g. in Belgium the yield of wheat per acre is double that obtained in India.

In India not a single firm exists for the fixation of the nitrogen of the air and naturally ammonium salts manufactured in other countries have to be used for the soil, but the Indian peasant in general is too poor to utilise the imported and costly ammonium salts. They generally apply farmyard manure (cow-dung), oil-cakes, green manure, etc. All these substances contain proteins. The proteins are first converted into amino acids and ammonium salts, which in their turn combine with the oxygen of the air present in the soil forming nitrites. The nitrites are also oxidised to nitrates, which are the real nitrogenous plant food material. The plants absorb nitrates from the soil and utilise them for the building of proteins or nitrogenous compounds in their bodies. Ammonium salts are very seldom, and nitrites not at all, used up directly by plants.

We have after a series of researches extending over several years discovered an entirely new and at the same time an economical method for the conservation of the soil nitrogen and fixation of atmospheric nitrogen in the soil itself by the use of molasses and other carbonaceous substances. We have also investigated various factors which influence the nitrogen transformation and loss in the soil and have been able to elucidate the different stages in the nitrogen transformation in the soil.

Regarding the importance of the investigations on these problems, the Royal Commission on Agriculture in India (1928) reported as follows :—
' We have been impressed by the importance of research into the fundamental problems connected with losses in nitrogen and with nitrogen recuperation.' In the present communication a summary of our results and conclusions is recorded.

Fixation of nitrogen by the addition of molasses to soil in fields.

TABLE 1.

21,600 kilograms of molasses added per acre of land on 10-1-36.

Ammoniacal nitrogen.	Nitric nitrogen.	Available nitrogen.	Total nitrogen.	Total carbon.	Date of analysis.
0·00466%	0·0032%	0·0079%	0·0561%	0·628%	original.
0·0064	0·0037	0·01016	0·0636	2·55	10-1-36
0·0076	0·0028	0·0104	0·0748	2·06	17-2-36
0·0077	0·0037	0·0114	0·0758	1·921	3-3-36
0·0076	0·0037	0·0113	0·0759	1·912	13-3-36
0·0087	0·0026	0·0113	0·0781	1·852	4-4-36
0·0087	0·0036	0·0124	0·0782	1·844	25-4-36
0·0026	0·0041	0·0068	0·0603	1·012	17-7-36

(The last series of results were obtained after heavy rains).

TABLE 2.

42,200 kilograms of molasses added per acre of land on 10-1-36.

Ammoniacal nitrogen.	Nitric nitrogen.	Available nitrogen.	Total nitrogen.	Total carbon.	Date of analysis.
0·0046%	0·0032%	0·0079%	0·0561%	0·628%	original.
0·0052	0·0036	0·0088	0·0667	3·528	10-1-36
0·0066	0·0035	0·0102	0·0778	3·1026	17-2-36
0·0068	0·0035	0·0104	0·0782	2·652	3-3-36
0·0062	0·0036	0·0098	0·0783	2·582	13-3-36
0·010	0·0026	0·0126	0·0822	2·012	4-4-36
0·0104	0·0036	0·0140	0·0831	1·872	25-4-36
0·0031	0·0048	0·0079	0·070	1·214	17-7-36

(The last series of results were obtained after heavy rains.)

The foregoing results in Tables 1 and 2 show that there is an increase in the total nitrogen and ammonia contents when molasses is added to the soil. It will be found that the amount of ammonia decreases after a maximum has been reached. But at this stage the nitrate content increases appreciably due to the oxidation of ammonium salts formed by nitrogen fixation. When the amounts of molasses added to the soil are not large, the maximum is reached within two months. After this stage the nitrate increases due to the oxidation of the ammonium salts produced from the nitrogen fixation in the soil and there is a loss of the total available nitrogen and the carbon-nitrogen ratio approaches the value 11 : 1. Hence, when the nitrate content of the soil begins to increase appreciably, the soil is most suitable for the sowing of crops. When larger quantities of molasses are added to the soil in the fields more time is required to attain the stage of nitrate increase. ✓

Previous workers have not been able to obtain uniformly good results with molasses as a manure as will be evident from the following quotations :—

'Increased yields of sugarcane have followed the application of molasses to soils at the Station Agronomique and on Mr. Ebbel's estate in Mauritius where the residual effect is well shown, and also in Antigua. Peck in Hawaii, on the other hand, observed marked losses of nitrate, as also did Harrison in British Guiana.'

'Laboratory investigations in humid climates suffer from the difficulty that the soils already contain so much nitrogen that small changes are difficult to measure accurately, and there are losses of nitrogen which counter-balance any fixation. Investigation would be easier in some of the soils very poor in nitrogen found in hot, arid conditions. Rigid incontestable proof could be furnished only by a demonstrated gain in nitrogen effected by *Azotobacter*, all other possibilities being ruled out. This proof has not yet been forthcoming.' (Russell, 1932.)

'In view of the fact that the energy added to the soil is not directly available to the nitrogen-fixing bacteria and that small amounts of available nitrogen are always present in the soil and the error in the laboratory determination of total nitrogen by the Kjeldahl method is greater than the possible

amount of nitrogen fixed by non-symbiotic bacteria, we are still unable to decide the question definitely.' (Waksman, 1927.)

' Wide use is being made in systems of agriculture of the bacteria, which work with legumes, but the nitrogen fixing power of those which work outside the plant is as yet not utilised extensively by man, since the methods of controlling them are not well understood.' (Miller, 1924). A. Koch, J. Litzendorff, F. Krull, and A. Alves (1907) have reported nitrogen fixation in plates and pots with dextrose but Pfeiffer and Blanck (1912) could not obtain any nitrogen fixation with sugar. According to Hutchinson (1918) sugars show beneficial results in autumn but not in spring.

Dr. H. W. Kerr has reported the following yield of sugar-cane on applying 10 tons of molasses per acre in the Bundaberg farm in Queensland.

No molasses	..	..	..	22·7 tons per acre.
10 tons molasses	..	..	..	37·1 ,, ,, ,,

On the other hand, Crabtree working in the Fairy Mead farm in Queensland did not find any beneficial effect with molasses. In the discussion, Dr. Kerr (1932) stated : ' The value of the molasses is probably due to its physical, chemical, and biological influences in the soil.' On applying molasses to the growing crop, no beneficial effect was obtained at Pusa. Recently, an increase of yield to the extent of 36 per cent has been reported at the Shahjehanpur Government Farm on applying 10,800 kg. of molasses per acre in the cultivation of sugar-cane, before planting. Messrs. Parry & Co., Ltd., of Madras have also obtained an increase of 40 per cent in the yield of sugar-cane. But when molasses was added to the growing crop, no beneficial result was obtained. We have observed that the energy liberated in the oxidation of the carbohydrates present in molasses either through the agency of bacteria or sunlight or induction or catalyst is utilised in the fixation of atmospheric nitrogen. Moreover, as molasses contains lime, potash, and phosphates, it should have a fertilising value. Previous workers determined only the total nitrogen of the soil after the addition of energy-rich compounds, and as the difference in total nitrogen is not very high before and after the addition of energy-rich compounds to the soil, they were doubtful regarding the fixation of nitrogen in the soil. But as both the available (ammoniacal and nitric nitrogen) and the total nitrogen have been estimated, we have been able to detect the increase of available nitrogen and also total nitrogen in all cases of well aerated soils. Using three tons of molasses per acre of land, we have obtained a fixation of 112 lbs. of nitrogen per acre.

The failure of previous workers to obtain definite evidence of fixation is due to the lack of oxidation of the energy-rich materials in the soil due to insufficiency of aeration or the low temperature of the soil.

The available and total nitrogen of soils, which have been molassed for three consecutive years, are greater than in soils molassed once or twice. It seems, therefore, that molasses exerts a residual effect on the soil.

Azotobacter FIXES NITROGEN VERY WELL IN TROPICAL SOILS.

In cold countries, the soil temperature being low and due to lack of sunshine, the velocity of the oxidation of energy-rich substances present in the molasses may be small and thus the energy available from the oxidation of carbohydrates may be too small for any marked nitrogen fixation. That is why many workers like Pfeiffer and Blanck, Hutchinson and others were unable to find beneficial effect with sugars. Moreover, in temperate climates, *Azotobacter* is not suitable for nitrogen fixation as the fixation at 10° and at lower temperature is practically nothing. The soil temperature in colder countries being lower than 10° most of the time in the year, practically no nitrogen fixation by *Azotobacter* is possible and that is why *Azotobacter* has not been utilised by agriculturists in cold countries. Thiele (1905) measured the soil temperatures of arable and grasslands daily for three years at Breslau, Germany, and reported that only rarely were they favourable for *Azotobacter*. Also *Azotobacter* requires more heat than *Bacillus radicicola* and several other bacteria and is eminently suitable for nitrogen fixation in tropical countries, except in the months of May and June, when the soil temperature during the daytime exceeds 50°, beyond which *Azotobacter* is unable to fix nitrogen. This bacteria should be widely used in the fixation of nitrogen in tropical countries when fed with energy-rich substances like molasses, pressmuds, cellulosic materials, etc. Recently Dhar and Tandon have measured the fixation of atmospheric nitrogen by pure cultures of *Azotobacter* thriving on mannite medium at 10°, 20°, 30°, 35°, 40°, 50°, 60°, and 70°. It has been observed that the maximum nitrogen fixation (largest amount of ammonium salt formation) takes place at 35°, which is, therefore, the optimum temperature for tropical *Azotobacter* as against 28° obtained in temperate countries. There is hardly any ammonia formation at 10° on the one hand and at 60° on the other. At 70° no nitrogen fixation by *Azotobacter* takes place. This is a very interesting case where the lower limit of bacterial activity is much higher than with the nitrite formers, *Bacillus radicicola* and several other bacteria. Moreover, the upper limit for *Azotobacter* is also appreciably higher. For example, even at 50° *Azotobacter* can fix an appreciable amount of nitrogen and the fixation at 45° is almost the same as at 20°. In the case of nitrite-formers, the bacterial activity ceases completely at 50°; even at 40° the activity of the nitrite formers is quite small in comparison to that at the optimum at 35°. These results show definitely that *Azotobacter* can stand high temperatures better than that of the nitrite formers and several other bacteria.

The optimum temperature for the nodule bacteria in temperate climates lies between 18° and 26° and is appreciably lower than that of *Azotobacter*. Moreover, *Bacillus radicicola* can thrive even at a temperature of 3° and that is why this bacteria has been utilised to a much greater extent in Europe and America than *Azotobacter*.

Molasses added to soil in heaps.   Composts with Molasses.

TABLE 3.

Heaps were made on 20th February, 1936.

(A) containing 80 kilograms of garden soil + 5 kilograms of molasses.
(B) ,,   ,,   ,,   ,,   ,,   ,,   +10   ,,   ,,   ,,
(C) ,,   ,,   ,,   ,,   ,,   ,,   +20   ,,   ,,   ,,
(D) ,,   ,,   ,,   *Usar* (alkali) soil + 5   ,,   ,,   ,,
(E) ,,   ,,   ,,   ,,   ,,   ,,   +10   ,,   ,,   ,,
(F) ,,   ,,   ,,   ,,   ,,   ,,   +20   ,,   ,,   ,,

The molasses contained 0·0021% ammoniacal nitrogen, 0·0001% nitric nitrogen, 0·577% total nitrogen and 55·2% carbon in an oven dried sample.

	Ammoniacal nitrogen	Nitric nitrogen	Total nitrogen	Total carbon	Date of analysis
Original garden soil	0·0028%	0·0032%	0·0583%	0·6525	20-2-36
Original *Usar* soil	0·0016	0·0016	0·0254	0·2907	,,
(A)	0·0060	0·0032	0·0933	2·612	5-3-36
(B)	0·0086	0·0030	0·1272	4·605	,,
(C)	0·0102	0·0027	0·175	8·604	,,
(D)	0·004	0·0016	0·0583	2·287	,,
(E)	0·0057	0·0016	0·0934	4·266	,,
(F)	0·0062	0·0015	0·1261	8·251	,,
(A)	0·0052	0·0032	0·10	2·082	27-3-36
(B)	0·0102	0·0026	0·14	3·823	,,
(C)	0·0162	0·0022	0·181	8·423	,,
(D)	0·0028	0·0016	0·0652	1·728	,,
(E)	0·007	0·0016	0·099	3·576	,,
(F)	0·0120	0·0014	0·1452	8·00	,,
(A)	0·0074	0·0032	0·1058	1·583	17-4-36
(B)	0·0124	0·0026	0·1468	3·012	,,
(C)	0·017	0·0022	0·1862	7·832	,,
(D)	0·0042	0·0016	0·0692	1·325	,,
(E)	0·0088	0·0016	0·1152	2·781	,,
(F)	0·01562	0·0015	0·1522	7·032	,,
(A)	0·0076	0·0032	0·1055	1·573	28-4-36
(B)	0·0126	0·0026	0·1428	2·879	,,
(C)	0·0174	0·0020	0·1858	7·253	,,
(D)	0·0045	0·0016	0·0712	1·125	,,
(E)	0·0097	0·0016	0·1212	2·622	,,
(F)	0·0156	0·0014	0·152	7·00	,,
(A)	0·0072	0·0039	0·1122	1·325	10-7-36
(B)	0·0087	0·0064	0·1672	1·922	,,
(C)	0·0114	0·0082	0·1987	3·246	,,
(D)	0·0050	0·0021	0·0785	0·885	,,
(E)	0·0093	0·0025	0·1428	1·5625	,,
(F)	0·0084	0·0057	0·1728	1·985	,,
(A)	0·0066	0·0036	0·112	1·312	25-8-36
(B)	0·0084	0·0062	0·1657	1·984	,,
(C)	0·0088	0·0078	0·1972	3·226	,,
(D)	0·005	0·0022	0·0778	0·895	,,
(E)	0·0086	0·005	0·1425	1·542	,,
(F)	0·0082	0·0051	0·1724	1·984	,,

Russell (Soil Conditions and Plant Growth, 1932, pp. 436-437) states : ' In neutral soils of cool countries *Bacillus radicicola* is the most active fixer of nitrogen and *Azotobacter* is relatively inactive. . . . .

' In alkaline soils of warm climates, on the other hand, *Azotobacter* is greatly stimulated ; *Bacillus radicicola* is not . . . . '

In tropical countries if the soil is ploughed after the addition of molasses, there is no reason why soil fertility regarding combined nitrogen should not be increased.

The above results show that when molasses is added to soil (normal or alkaline) in heaps and exposed to air and light, the available and total nitrogen are considerably increased. The total nitrogen is more than double that of the original amount present in the soil before the addition of molasses. Hence considerable fixation of nitrogen takes place and excellent composts are prepared with molassed soils, of which the carbon-nitrogen ratio becomes normal and attains the value of 11·5.

Nitrogen fixation and Azotobacter count on the application of Molasses, Carbohydrates, Starch, and Glycerol.

Dhar and Seshacharyulu (May, 1936) have investigated how the *Azotobacter* in soils under natural conditions will be affected by the application of molasses and whether there is any correlation between the *Azotobacter* numbers and the amount of fixation of atmospheric nitrogen.

Different amounts of molasses, 10 and 30 kilograms, were added to two equal plots of land of area 144 sq. ft. and a third plot of equal area was kept as control without the addition of molasses. The *Azotobacter* count and the nitrogen estimations (ammoniacal, nitric and total nitrogen) of all the three plots were made before the addition of molasses and afterwards at regular intervals. The plots were dug up twice a month and the same amount of water was added to the three plots at the same time. The soil in all the experiments was taken from depths varying from zero to nine inches. A random sampling was made from 40 to 50 places in each plot. *Azotobacter* counts were made by the plate method using Beijerinck's mannite medium to which 2% agar was added.

TABLE 4.

Plot containing 30 kilograms of molasses.

Date.	Ammoniacal nitrogen %	Total nitrogen %	Number of Azotobacter in millions per 1 gm. of dry soil	
22-10-35	. . . .	. . . .	6·4	Nitric nitrogen varied from 0·00396% to 0·00464%.
26-10-35	0·00221	0·0953	6·6	
3-11-35	0·00247	0·0953	4·7	
11-11-35	0·00266	0·0966	57·7	
15-11-35	0·00273	0·0966	5830·0	
22-11-35	0·0028	0·0966	5960·0	
30-11-35	0·002904	0·0976	5040·0	
7-12-35	0·00305	0·1	25600·0	
18-12-35	0·00373	0·1024	27600·0	
29-12-35	0·003904	0·1036	27500·0	
18-1-36	0·0042	0·1076	22600·0	
5-2-36	0·00448	0·1076	25400·0	
12-3-36	0·003904	0·1036	1410·0	

TABLE 5.

Plot containing 10 kilograms of molasses.

Date	Ammoniacal nitrogen %	Total nitrogen %	Number of Azotobacter in millions per 1 gm. of dry soil	
22-10-35	. . . .	. . . .	5·1	Nitric nitrogen varied from 0·00339% to 0·0037%.
26-10-35	0·00155	0·088	5·2	
3-11-35	0·0024	0·0884	17·9	
11-11-35	0·00285	0·0912	17·7	
15-11-35	0·0029	0·0912	16·4	
22-11-35	0·00305	0·0932	16·8	
30-11-35	0·00287	0·0932	17·2	
7-12-35	0·00284	0·0932	17·8	
18-12-35	0·00284	0·0932	22·2	
29-12-35	0·00282	0·0922	20·4	
18-1-36	0·0028	0·0922	21·0	
5-2-36	0·0028	0·0922	22·6	
12-3-36	0·0024	0·0912	10·7	

TABLE 6.

Control plot.

Date	Ammoniacal nitrogen %	Total nitrogen %	Number of Azotobacter in millions per 1 gm. of dry soil	
22-10-35	....	....	2·3	Nitric nitrogen varied from
26-10-35	0·00124	0·082	2·3	0·00304% to 0·00288%.
3-11-35	0·0013	0·08	2·0	
11-11-35	0·001216	0·0792	2·7	
15-11-35	0·001216	0·0792	2·3	
22-11-35	0·001216	0·0792	2·5	
30-11-35	0·001216	0·0792	2·3	
7-12-35	0·001216	0·0792	2·6	
18-12-35	0·001216	0·0792	2·8	
29-12-35	0·001216	0·0792	2·5	
18-1-36	0·001216	0·0792	2·1	
5-2-36	0·001216	0·0792	2·6	
12-3-36	0·0012	0·078	1·8	

From the foregoing results it is clear that *Azotobacter* numbers in the soil increase in abundance on the application of molasses and reach a maximum, where they remain more or less stationary, but the rate at which they develop is not proportional to the nitrogen fixed. Another interesting fact is that whenever there was an increased fixation of ammoniacal nitrogen there was almost a steadiness in the bacterial numbers. This fact leads us to the conclusion that fixation of atmospheric nitrogen is not mainly bacterial but is aided by other agencies. Moreover, in the case of the plot containing 30 kilograms of molasses, we observe that there was a slight decrease in the *Azotobacter* numbers in the beginning compared to the blank, though there was an increase in the ammoniacal nitrogen. These facts go to show that there is no real correlation between the *Azotobacter* numbers and soil nitrogen increase. The *Azotobacter* develop abundantly on the addition of molasses to the soil and thus help in the nitrogen fixation in addition to the photochemical, induced or catalytic oxidations going on simultaneously. Another important fact is that not only the available nitrogen but also the total nitrogen of the soil increases considerably by the application of molasses. No appreciable change either in the *Azotobacter* numbers or nitrogen content of the control plot is observed.

Nitrogen fixation and Azotobacter count on the addition of cane sugar and glucose to the soil in basins.

In order to investigate further whether the fixation of atmospheric nitrogen in tropical soils is mainly a bacterial one or due also to photochemical and other agencies, experiments were done by the above authors by adding cane sugar and glucose to the soil in basins and exposing them to the sunlight.

1000 gms. of garden soil were mixed with 20 gms. of cane sugar or glucose and 300 c.c. of water in enamelled basins and exposed to the sunlight daily for seven hours.   Some basins with the same substances were kept in a dark room in order to exclude light.   In one set of the experiments 2 gms. of calcium carbonate were added.   160 c.c. of water were added twice a day to the exposed basins and 160 c.c. of water to the basins kept in the dark after every three days for maintaining an uniform moisture content.   Before the commencement of the experiment estimations of nitrogen, total carbon, and *Azotobacter* numbers of the original soil were done.   At regular intervals, the nitrogen content, total carbon, and *Azotobacter* counts of the exposed and dark basins were determined.

The following results were obtained :—

TABLE 7.

1 kilogram of soil +2 gms. calcium carbonate +20 gms. cane sugar.

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
30-12-1935 original soil	0·00124	0·0433	0·4677	12·5	Nitric nitrogen
13-1-36	0·00152	0·0433	....	8·0	varied from
30-1-36	0·00215	0·0442	1·0356	9·3	0·00316% to
15-2-36	0·00364	0·0488	0·866	11·3	0·0036%.
29-2-36	0·00464	0·0506	0·713	18·3	
16-3-36	0·00552	0·051	0·606	18·8	
31-3-36	0·00488	0·0506	0·563	13·2	
14-4-36	0·00392	0·0506	0·557	14·6	

TABLE 8.

1 kilogram of soil +20 gms. cane sugar.

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
30-12-1935 original soil	0·00124	0·0433	0·4677	12·5	Nitric nitrogen
13-1-36	0·00143	0·0433	....	6·0	varied from
30-1-36	0·00205	0·0442	1·0401	7·9	0·003168% to
15-2-36	0·0035	0·0482	0·866	10·3	0·0036%.
29-2-36	0·00436	0·05	0·718	19·2	
16-3-36	0·00524	0·0506	0·602	18·2	
31-3-36	0·00476	0·05	0·552	17·1	
14-4-36	0·0038	0·05	0·549	16·2	

TABLE 9.

1 kilogram of soil +2 gms. calcium carbonate +20 gms. cane sugar.

Dark.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
30-12-1935 original soil	0·00124	0·0433	0·4677	12·5	Nitric nitrogen
13-1-36	0·00126	0·0433	....	9·5	varied from
30-1-36	0·00157	0·0433	1·1383	33·7	0·003168% to
15-2-36	0·00215	0·0456	1·028	175·0	0·00325%.
29-2-36	0·00288	0·0472	0·928	250·0	
16-3-36	0·0032	0·0472	0·837	375·0	
31-3-36	0·00372	0·0488	0·696	415·0	
14-4-36	0·0036	0·0488	0·618	395·0	

TABLE 10.

1 kilogram of soil +20 gms. cane sugar.

Dark.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
30-12-1935 original soil	0·00124	0·0433	0·4677	12·5	Nitric nitrogen
13-1-36	0·00125	0·0433	....	7·4	varied from
30-1-36	0·00152	0·0433	1·1494	28·8	0·003168% to
15-2-36	0·0021	0·0456	1·028	170·0	0·00325%.
29-2-36	0·00288	0·0472	0·922	245·0	
16-3-36	0·00336	0·0472	0·832	364·0	
31-3-36	0·0038	0·0488	0·698	420·0	
14-4-36	0·00372	0·0488	0·614	400·0	

TABLE 11.

1 kilogram of soil +2 gms. calcium carbonate +20 gms. glucose.

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
4-2-1936 original soil	0·00123	0·0433	0·4677	11·2	Nitric nitrogen
22-2-36	0·00168	0·0433	1·1734	10·2	varied from
7-3-36	0·0028	0·046	1·0014	18·8	0·003168% to
21-3-36	0·00348	0·0488	0·836	17·3	0·00382%.
7-4-36	0·0044	0·05	0·691	15·4	
21-4-36	0·00372	0·05	0·638	15·8	
7-5-36	0·00336	0·0488	0·586	15·1	
21-5-36	0·0032	0·0488	0·526	15·6	
7-6-36	0·00305	0·0488	0·518	15·0	

TABLE 12.

1 kilogram of soil +20 gms. glucose.

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
4-2-1936 original soil	0·00123	0·0433	0·4677	11·2	Nitric nitrogen
22-2-36	0·00166	0·0433	1·1778	9·9	varied from
7-3-36	0·0028	0·0456	1·0014	17·4	0·003168% to
21-3-36	0·00336	0·0477	0·842	16·3	0·0039%.
7-4-36	0·00452	0·05	0·694	16·8	
21-4-36	0·00388	0·05	0·642	16·1	
7-5-36	0·00343	0·0488	0·591	16·2	
21-5-36	0·00336	0·0488	0·526	16·1	
7-6-36	0·00305	0·0488	0·518	16·5	

TABLE 13.

1 kilogram of soil +2 gms. calcium carbonate + 20 gms. glucose.

Dark.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
4-2-1936 original soil	0·00123	0·0433	0·4677	11·2	Nitric nitrogen varied from 0·003168 % to 0·00328%.
22-2-36	0·00142	0·0433	1·2056	18·5	
7-3-36	0·00168	0·0433	1·1232	36·5	
21-3-36	0·00204	0·0456	1·0221	168·0	
7-4-36	0·00258	0·0466	0·906	232·0	
21-4-36	0·0029	0·0466	0·8074	315·0	
7-5-36	0·00329	0·0472	0·6748	390·0	
21-5-36	0·003	0·0472	0·6127	365·0	
7-6-36	0·0029	0·0472	0·5636	325·0	

TABLE 14.

1 kilogram of soil + 20 gms. glucose.

Dark.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
4-2-1936 original soil	0·00123	0·0433	0·4677	11·2	Nitric nitrogen varied from 0·003168 to 0·00328%.
22-2-36	0·0014	0·0433	1·2016	18·0	
7-3-36	0·00164	0·0433	1·1224	37·5	
21-3-36	0·0021	0·0456	1·021	170·0	
7-4-36	0·00254	0·0466	0·908	228·0	
21-4-36	0·0028	0·0466	0·8078	320·0	
7-5-36	0·00323	0·0472	0·6662	395·0	
21-5-36	0·00305	0·0472	0·6088	350·0	
7-6-36	0·00294	0·0466	0·5546	345·0	

The above results show that although the *Azotobacter* numbers in the basins exposed to sunlight for 7 hours daily are much less, the amount of ammonia and total nitrogen are greater than in those kept in the dark. Moreover, the amount of carbon in the exposed basins are less than in those kept in the dark. Hence in presence of sunlight the oxidation of substances like canesugar and glucose is greatly facilitated and causes the fixation of nitrogen in greater

amounts than in the dark. It is clear, therefore, that in the presence of light the photochemical oxidation of energy-rich substances can cause nitrogen fixation just as the bacterial fixation does under ordinary conditions. Therefore, along with bacterial fixation of nitrogen in tropical soils there is considerable fixation due to the photochemical oxidation of energy-rich substances and that is why, although the number of *Azotobacter* in the basins receiving sunlight is much less than in the basins kept in the dark, the ammonia and total nitrogen contents are greater than in the dark ones.

It may be argued that when the basins are exposed to the light the temperature of the soil is increased and this leads to an increased activity of *Azotobacter* and hence an increase in the nitrogen fixation. The temperature of the basins receiving sunlight varied from 40°–44°, whereas the dark room temperature varied from 25°–30°. In a previous paper, Dhar and Tandon (*Proc. National Academy of Sciences, India*, 1936, *6*, 35) have reported that the optimum temperature for *Azotobacter* is 35° and the fixation at 45° is practically the same as at 20°. Hence the nitrogen fixation due to *Azotobacter* alone should be practically identical in the basins kept in the dark room or receiving sunlight. In order to test this point further, 200 gms. of the garden soil mixed with 2 gms. of glucose and 32 c.c of water were incubated at 32°–33°. Exactly another basin was exposed to sunlight.

The temperature of the exposed basin varied from 42°–44°. To the exposed one 32 c.c. of water were added twice a day and to the incubated one 32 c.c. after every five days in order to keep the moisture content the same. Both the soils were analysed simultaneously on the following dates recorded in the table.

TABLE 15.

Exposed to sunlight.

Date	Ammoniacal nitrogen	Total nitrogen	Total carbon	Number of Azotobacter in millions per 1 gm. of dry soil
10-3-36 original soil	0·00108	0·042	0·441	7·2
1-4-36	0·0024	0·00446	0·619	12·5
11-4-36	·0·00304	0·00456	0·511	15·7
Incubated.				
1-4-36	0·00186	0·0437	0·684	31·8
11-4-36	0·00214	0·0442	0·602	45·0

The above results show that although the soil is incubated at 32°-33°, which is very near the optimum for *Azotobacter*, yet the ammonia and total

nitrogen contents of the one incubated are less than that exposed, whose temperature while receiving sunlight is 42°–44°. It appears, therefore, that the greater nitrogen fixation in presence of light is chiefly due to the photo-oxidation of the energy-rich compounds.

The size of the colonies developed on the plates containing the incubated soil are much bigger than those obtained from the exposed one. In the soils kept in the dark the colonies are also appreciably bigger than the colonies obtained from the soils receiving sunlight. A tentative suggestion may be offered as to the reason of the difference in size that the generation time of those kept in the dark and also incubated at 32°–33° is less compared to those exposed, probably sunlight inhibiting the growth. If bacterial metabolic activity is considered to go hand in hand with the growth activity, the fixation of atmospheric nitrogen in the incubated and dark basins should have been more than the ones exposed, if no other agent was responsible in nitrogen fixation. Therefore in tropical soils, along with bacterial fixation, photochemical fixation seems to play a prominent rôle.

An interesting point can be deduced from our observations that the fixation is not much affected by the presence of calcium carbonate. This behaviour is due to the fact that soils with which we carried on our experiments are rich in calcium.

Similar experiments are in progress with starch, glycerol, mannitol, and mixture of molasses and soil in heaps. In the case of the starch, sugars were detected both in the exposed and dark basins. The following results were obtained.

TABLE 16.

1 kilogram of soil +50 gms. starch.

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
10-3-1936 original soil	0·00108	0·042	0·441	7·2	Nitric nitrogen varied from 0·0024% to 0·00262.
9-4-36	0·00109	0·042	....	6·8	
30-4-36	0·00184	0·0433	2·4425	8·2	
20-5-36	0·00232	0·0442	2·37	9·1	
20-6-36	0·00294	0·0451	2·2765	15·6	
16-7-36	0·00336	0·0461	2·1753	19·8	
28-7-36	0·00372	0·0472	2·0932	28·2	
7-10-36	0·0052	0·051	1·4411	38·6	
7-11-36	0·0056	0·053	1·2592	31·2	

TABLE 17.

1 kilogram of soil + 50 gms. starch.

Dark.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
10-3-1936 original soil	0·00108	0·042	0·441	7·2	Nitric nitrogen varied from 0·0024% to 0·0025.
9-4-36	0·00108	0·042	....	8·1	
30-4-36	0·0014	0·042	2·5182	11·2	
20-5-36	0·00152	0·042	2·4761	18·5	
20-6-36	0·00184	0·0433	2·4137	26·8	
16-7-36	0·0021	0·0437	2·3352	46·0	
28-7-36	0·00232	0·0442	2·2654	98·6	
7-10-36	0·0031	0·0461	1·8286	205·5	
7-11-36	0·0032	0·0461	1·7164	265·0	

TABLE 18.

1 kilogram of soil + 50 gms. glycerol.

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
10-3-1936 original soil	0·00108	0·042	0·441	7·2	Nitric nitrogen varied from 0·0024% to 0·00258%.
7-4-36	0·00168	0·042	2·2726	9·1	
3-5-36	0·00232	0·0442	2·1737	9·7	
29-5-36	0·00294	0·0451	2·0314	12·5	
18-6-36	0·0034	0·0451.	1·9188	21·5	
16-7-36	0·00364	0·0456	1·8123	27·0	
29-7-36	0·00388	0·0461	1·7311	30·8	
7-10-36	0·00464	0·0482	1·2685	36·2	
3-11-36	0·00508	0·05	1·0952	32·1	

TABLE 19.

1 kilogram of soil +·50 gms. glycerol.

Dark.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
10-3-1936 original soil	0·00108	0·042	0·441	7·2	Nitric nitrogen 0·0024% is constant.
7-4-36	0·00134	0·042	2·3354	12·2	
3-5-36	0·00176	0·0428	2·267	22·7	
29-5-36	0·00208	0·0437	2·1838	68·0	
18-6-36	0·00232	0·0437	2·1066	86·5	
16-7-36	0·00258	0·0437	2·0164	98·5	
29-7-36	0·00264	0·0442	1·9582	128·6	
7-10-36	0·003	0·0451	1·6544	215·4	
3-11-36	0·0031	0·0451	1·561	286·0	

TABLE 20.

1 kilogram of soil +20 gms. mannitol.

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
20-4-1936 original soil	0·00152	0·043	0·494	6·5	Nitric nitrogen varied from 0·00308% to 0·0032%.
5-5-36	0·002	0·043	1·2087	11·8	
22-5-36	0·0028	0·0454	1·0725	16·6	
8-6-36	0·0035	0·0472	0·9539	20·5	
24-6-36	0·00436	0·0489	0·8118	28·5	
14-7-36	0·005	0·0506	0·7156	32·5	
26-7-36	0·00536	0·051	0·6432	29·8	
10-8-36	0·0052	0·051	0·5846	30·5	

TABLE 21.

1 kilogram of soil +20 gms. mannitol.

Dark.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
20-4-1936 original soil	0·00152	0·043	0·494	6·5	Nitric nitrogen 0·00308 is constant.
5-5-36	0·00174	0·043	1·2266	17·5	
22-5-36	0·00207	0·043	1·1654	29·2	
8-6-36	0·00252	0·0454	1·0912	110·0	
24-6-36	0·00294	0·0454	1·0091	175·0	
14-7-36	0·00341	0·0466	0·9299	235·0	
26-7-36	0·00368	0·0472	0·8516	292·6	
10-8-36	0·00384	0·0477	0·7634	355·8	

TABLE 22.

Heap (80 kg. of soil +10 kilograms of molasses).

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
4-4-1936 original soil	0·0014	0·0365	0·431	8·6	Nitric nitrogen 0·0024% is constant.
21-4-36	0·007	0·1	3·8642	0·3	
5-5-36	0·00932	0·1076	3·5931	3·6	
25-5-36	0·0112	0·112	3·3511	8·4	
14-6-36	0·0127	0·114	3·0707	19·6	

TABLE 23.

Heap (80 kg. of soil +10 kilograms of molasses).

Dark.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
4-4-1936 original soil	0·0014	0·0365	0·431	8·6	Nitric nitrogen
21-4-36	0·00404	0·0932	4·0232	0·9	0·0024% is
5-5-36	0·0056	0·096	3·8704	10·0	constant.
25-5-36	0·007	0·1014	3·7222	25·5	
14-6-36	0·008	0·1014	3·6033	48·5	

In order to find out whether the above conclusion, namely photochemical fixation of atmospheric nitrogen in tropical soils, holds good in fields the following experiments were also performed in fields :—

Six plots of equal area (6'×4') were taken. To one set of 2 plots 10 kilograms of molasses were added and to another set of 2 plots 5 kilograms were added. The remaining 2 plots were kept as control. One plot from each set was covered with wooden planks on raised bricks in order to exclude sunlight and the other plots were exposed. The exposed plots were watered after every 4 days and dug up and the covered plots were watered once a week but dug up simultaneously with the exposed plots. At regular intervals the *Azotobacter* count and nitrogen estimations of all the plots were carried on. The temperature of the exposed plots during the months of April, May and June varied from 59°·5 to 38° at depths varying from 1 to 6 inches and that of the covered plots from 41° to 31°·5 at the same depths.

The following results were obtained :—

TABLE 24.

Plot (6′ × 4′) containing 5 kilograms of molasses.

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
14-4-1936 original soil	0·00175	0·0874	0·7858	2·1	Nitric nitrogen
27-4-36	0·00244	0·0874	1·2054	10·5	of the plot
9-5-36	0·00328	0·09	1·1326	32·0	varied from
21-5-36	0·00388	0·092	1·0474	40·5	0·00311% t o
31-5-36	0·00432	0·0932	1·0021	48·5	0·0035%.
16-6-36	0·00444	0·094	0·9693	42·0	
17-7-36	0·004	0·094	0·9562	49·5	
15-10-36	0·0031	0·0932	0·9411	30·5	

TABLE 25.

Plot (6′ × 4′) containing 5 kilograms of molasses.

Covered.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
14-4-1936 original soil	0·002	0·094	0·8648	1·9	Nitric nitrogen
27-4-36	0·00233	0·094	1·3376	21·2	of the plot
9-5-36	0·0028	0·094	1·2052	45·0	0·00294% is
21-5-36	0·00308	0·096	1·2331	55·0	constant.
31-5-36	0·00328	0·0978	1·1945	62·0	
16-6-36	0·00368	0·0978	1·1347	90·0	
17-7-36	0·00388	0·0978	1·0504	115·0	
15-10-36	0·00292	0·096	0·9824	56·2	

TABLE 26.

Plot (6' × 4') containing 10 kilograms of molasses.

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
11-4-1936 original soil	0·00236	0·08	0·7332	2·1	Nitric nitrogen of the plot
23-4-36	0·0028	0·08	1·5364	4·3	varied from
6-5-36	0·00348	0·0822	1·4642	23·5	0·0035% to
17-5-36	0·004	0·0832	1·389	32·5	0·00352%.
28-5-36	0·00432	0·0848	1·327	40·0	
15-6-36	0·005	0·0864	1·246	72·5	
16-7-36	0·0056	0·0878	1·1216	88·5	
4-8-36	0·004	0·0864	1·0014	82	After heavy rains.
18-10-36	0·00308	0·0864	0·9624	50·2	

TABLE 27.

Plot (6' × 4') containing 10 kilograms of molasses.

Covered.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
11-4-1936 original soil	0·00208	0·0932	0·9207	2·6	Nitric nitrogen of the plot
23-4-36	0·00236	0·0932	1·7419	5·8	0·0035% is
6-5-36	0·00274	0·094	1·6919	34·5	constant.
17-5-36	0·00294	0·094	1·6334	43·0	
28-5-36	0·00308	0·0958	1·5872	50·5	
15-6-36	0·0034	0·0964	1·5234	86·0	
16-7-36	0·00388	0·0964	1·4236	135·0	
4-8-36	0·00308	0·0958	1·2036	88	After heavy rains.
18-10-36	0·00274	0·094	0·9824	62·0	

TABLE 28.

Control plot (6′ × 4′).

Exposed.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
16-4-1936	0·00175	0·1	0·903	2·4	Nitric nitrogen
28-4-36	0·00175	0·1	0·903	2·6	of the plot
11-5-36	0·00175	0·1	0·903	1·6	varied from
22-5-36	0·00175	0·1	0·903	1·7	0·00328% to
1-6-36	0·00169	0·0986	0·903	1·8	0·00333%.
16-6-36	0·00169	0·0986	0·903	2·1	
18-7-36	0·00169	0·0986	0·903	2·9	
20-10-36	0·00169	0·0986	0·903	2·7	

TABLE 29.

Control plot (6′ × 4′).

Covered.

Date	Ammoniacal nitrogen %	Total nitrogen %	Total carbon %	Number of Azotobacter in millions per 1 gm. of dry soil	
16-4-1936	0·00184	0·0902	0·8344	2·03	Nitric nitrogen
28-4-36	0·00184	0·0902	0·8344	2·8	of the plot
11-5-36	0·00184	0·0902	0·8344	2·4	0·00328% is
22-5-36	0·00184	0·0902	0·8344	2·3	constant.
1-6-36	0·00184	0·0902	0·8344	2·6	
16-6-36	0·001804	0·0876	0·8344	2·9	
18-7-36	0·001804	0·0876	0·8344	3·0	
20-10-36	0·001804	0·0876	0·8344	3·1	

The foregoing results clearly substantiate the conclusion that in tropical soils along with bacterial fixation, photochemical fixation of atmospheric nitrogen is prominent. Another point we have observed is that the greater the total nitrogen of the original soil the smaller the amount of nitrogen fixed on the addition of molasses.

PROBABLE MECHANISM OF NITROGEN FIXATION.

It is believed that under both anaerobic and aerobic conditions, ammonia is the first product of nitrogen fixation, as ammonia is easily detected in the fixation of atmospheric nitrogen. Glucose has been found to decompose into pyruvic acid and hydrogen under anaerobic conditions according to the equation :—$C_6H_{12}O_6 = 2CH_3COCOOH + 2H_2 + 12$ Cal. In presence of the nitrogen of the atmosphere and on the soil surface, the hydrogen obtained from the decomposition of glucose may form ammonia according to the equation :—$N_2 + 3H_2 = 2NH_3 + 24$ Cal.

In presence of oxygen, however, that is, under aerobic conditions, it is difficult to assume that ammonia is also the first product of nitrogen fixation. Because, in presence of oxygen, glucose can undergo one or more of the following oxidations on the soil surface :—

(1) $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O + 676$ Cal.

(2) $C_6H_{12}O_6 + 4\frac{1}{2}O_2 = 3C_2H_2O_4 + 3H_2O + 493$ Cal.

(3) $C_6H_{12}O_6 + 1\frac{1}{2}O_2 = C_6H_8O_7 + 2H_2O + 199$ Cal.

(4) $C_6H_{12}O_6 + O_2 = C_6H_{10}O_7 + H_2O + x$ Cal.

(5) $C_6H_{12}O_6 + \frac{1}{2}O_2 = C_6H_{12}O_7 + x$ Cal.

It seems that in the presence of air, the first change (1) is the most important. The above organic acids, which may be produced under aerobic conditions, and the organic acids (e.g., acetic, propionic, butyric, lactic, etc.) and traces of alcohol, glycerol, etc., which may be generated in anaerobic conditions, are also easily oxidised to carbonic acid on the soil surface liberating energy. Hence, a large quantity of energy is available on the soil surface for nitrogen fixation on the addition of molasses or cane sugar to soil exposed to air and light.

We have shown that ammonium salts are also produced in the photochemical or induced oxidation of carbohydrates in the complete absence of bacteria. Hence in the soil containing compounds of iron, manganese, traces of titanium, copper, etc. which are excellent catalysts in oxidation reactions and exposed to sunlight and air, the oxidation of the carbohydrates added with molasses is certainly due to bacteria, light and chemical catalysts all acting simultaneously. For obtaining the hydrogen required for ammonia formation, the following reaction has to take place :—$H_2O = H + OH - 112$ Cal. The direct combination of nitrogen and oxygen forming nitric oxide, according to the equation : $N_2 + O_2 = 2NO + 43\cdot2$ Cal., appears to require less energy than the process leading to the formation of ammonia. It appears that the iron compounds, traces of manganese and copper compounds, and sunlight, which falls on the soil surface, can facilitate the formation of nitric oxide from oxygen and nitrogen of the air. The nitric oxide can be readily oxidised to nitrous and nitric acids, which form nitrates in the soil.

Dhar and Mukerji (1934) have shown that solutions of nitrates and carbohydrates in presence of sunlight and titanium oxide (TiO_2) can readily form small amounts of amino acids, with copious production of ammonium

salts. It is interesting to note that ammonium salts and carbohydrates when exposed to the sunlight in presence of titanium oxide do not, however, form amino acids. It is well known that in plants the proteins, which are mostly the condensation products of amino acids, are only formed when carbohydrates have already accumulated by photosynthesis. The carbohydrates formed by photosynthesis in plants react with nitrates absorbed by plants from the soil and this results in the production of amino acids, proteins and ammonium salts in the plants. As a matter of fact, Waynick and Woodhouse (1918–19) have obtained evidence of amino acid formation in nitrogen fixation by *Azotobacter*. It is believed that in the first few days of the growth of *Azotobacter* amino acids accumulate and later on proteins increase. In our experiments with pure cultures of *Azotobacter* thriving in mannite we have been able to detect amino acids, by the valuable ' ninhydrin ' test in the filtered liquids obtained by crushing the *Azotobacter* cells with sand in a pestle and mortar. According to Jodidi (1910), Schreiner and Skinner (1912), and Lathorp (1917), several amino acids are of common occurrence in the soil. These amino acids may be obtained either by the hydrolysis of proteins added to the soil as manure or formed synthetically as explained above. It seems likely, therefore, *in vitro* as well as in the plant and in the soil, the nitrate is reduced to ammonia by the action of carbohydrates or other carbonaceous compounds with simultaneous formation of amino acids in small quantities. Hence, it appears that nitrates are first produced in nitrogen fixation and the nitrates react with the energy-rich materials present in the soil with the formation of ammonium salts and small amounts of amino acids.

No Anaerobic Denitrification on the Addition of Molasses to Fields.

Our field experiments as well as those carried on in dishes show that there is absolutely no anaerobic denitrification even when large quantities of molasses are added to soil exposed to air and light. The available nitrogen (sum of ammoniacal and nitric nitrogen) and the total nitrogen contents of the soil are never less than the original amounts present in the soil before the addition of molasses. As a matter of fact, even a few days after the addition of molasses to the soil, the ammoniacal nitrogen is appreciably increased and the available and total nitrogen contents also augment due to fixation of atmospheric nitrogen. When the amounts of molasses are large and the aeration of the soil inadequate, a part of the nitric nitrogen of the soil may be converted into ammoniacal nitrogen but it is never lost to the soil. The ammoniacal nitrogen in course of time is again oxidised to nitrate. This is a very important observation, which differs from the experience of workers in temperate climates. It has already been emphasised that the fixation of atmospheric nitrogen depends on the velocity of the oxidation of the energy-rich materials added to the soil, and due to the sunlight and the high temperature prevalent in tropical

soils, the oxidation of the carbohydrates and other energy-rich compounds is much greater than in colder countries and hence, in tropical countries, the soil condition from the view point of oxidation reactions are much more favourable than in temperate climates. Hence molasses even in large amounts when added to tropical soils, which are well aerated, always adds nitrogen to the soil and thus acts as an excellent fertiliser to crops and the question of anaerobic nitrogen loss from tropical soils does not arise.

Moreover, our experiments on compost formation with molasses show that the total nitrogen in the composts is double the amount originally present in the soil. The soil organic matter and humus and carbon are also considerably increased on the addition of molasses. Hence the increased nitrogen is stored in the soil and is available to plants, the soil organic matter acts as a preserver of the nitrogen. In a recent publication (1936) we have shown that the percentages of available nitrogen in tropical soils are greater than in those of temperate climates. Hence the total nitrogen which is added to the soil, due to nitrogen fixation on the addition of molasses, can partially be converted into the available form for absorption by plants. Due to the increase of carbon in the soil on the addition of molasses, the increased amounts of nitrogen arising out of fixation are well preserved, as it has been proved in our experiments that molasses can preserve the nitrogen added to the soil as ammonium sulphate. Hence molasses, which adds both carbon and nitrogen to tropical soils, is a distinctly better fertiliser for tropical soils than ammonium sulphate. On the addition of molasses to fields in two consecutive years there is a definite residual effect. When large amounts of molasses are added, the residual effect may last for more than two years. Hence molasses has several advantages over artificial nitrogenous manures.

Another interesting fact that has been brought out by our researches is that no flies or insects are attracted and no bad smell is given off even when 500 to 1,000 maunds of molasses are added per acre of land exposed to light and air. It is well-known that the soil surface is an excellent adsorbent. The organic substances and the products of their decomposition are readily adsorbed by the soil and they undergo decomposition and oxidation readily into carbon dioxide and water and ammonia when the soil is properly aerated. Hence molasses is a very suitable fertiliser for tropical countries, as it easily adds both combined nitrogen and humus, which are the crying need of tropical soils.

Under temperate conditions, it is well known that the addition of carbohydrate-rich material to soil tends to reduce the amount of nitrogen available to plants, the nitrogen becoming fixed as microbial protoplasm or as humus. In tropical conditions, however, the available nitrogen is not reduced at all even when large doses of carbohydrates are added to tropical soils.

We have applied molasses to more than 30 plots of land in different portions of the University compound and other places and we have always observed a marked increase in the ammonia and total nitrogen content of the soils on the application of molasses. In most of our field experiments the amount

TABLE 30.

Nitrogen fixation in soils with cellulosic substances, cow-dung, etc.

		Amount originally present on 16-4-36.	Exposed to sunlight.			Kept in diffused light.		
			on 5-5-36.	on 8-7-36.	on 11-8-36.	on 5-5-36.	on 8-7-36.	on 11-8-36.
500 g. soil + 25 g. Filter paper	NH₃-N =	0·0015%	0·0019%	0·0028%	0·0031%	0·0019%	0·0023	0·0024
	NO₃-N =	0·0029	0·0034	0·0041	0·0026	0·0034	0·0041	0·0025
	Total N =	0·0626	0·0752	0·0875	0·0886	0·0752	0·0834	0·0844
500 g. soil + 25 g. Filter paper + 5 g. Molasses	NH₃-N =	0·0015	0·0029	0·0030	0·0036	0·00216	0·0034	0·0035
	NO₃-N =	0·0029	0·0034	0·0036	0·0028	0·0034	0·0038	0·0027
	Total N =	0·0626	0·0752	0·100	0·101	0·0752	0·0934	0·0944
500 g. soil + 100 g. Dry leaves	NH₃-N =	0·00436	0·0043	0·0048	0·0058	0·004	0·0044	0·0046
	NO₃-N =	0·0040	0·0062	0·0077	0·0054	0·0062	0·0064	0·0056
	Total N =	0·1362	0·175	0·185	0·200	0·175	0·175	0·1922
500 g. soil + 100 g. Dry leaves + 5 g. Molasses	NH₃-N =	0·0043	0·007	0·0048	0·0063	0·0045	0·0042	0·0056
	NO₃-N =	0·0040	0·0062	0·0076	0·007	0·0062	0·0057	0·0062
	Total N =	0·1362	0·1738	0·200	0·234	0·175	0·188	0·2198
500 g. soil + 100 g. Leaf juice	NH₃-N =	0·0059	0·0058	0·0044	0·0031	0·0057	0·0052	0·0048
	NO₃-N =	0·0099	0·0046	0·0054	0·0043	0·0046	0·0043	0·0044
	Total N =	0·1093	0·112	0·119	0·116	0·112	0·112	0·114
500 g. soil + 100 g. Leaf juice + 5 g. Molasses	NH₃-N =	0·0059	0·0067	0·0041	0·0028	0·0058	0·0042	0·0042
	NO₃-N =	0·0099	0·0046	0·0037	0·004	0·0046	0·0037	0·0042
	Total N =	0·1093	0·112	0·148	0·152	0·112	0·138	0·142

		Amount originally present on 27-7-36.	Exposed to sunlight to 18-8-36.	Kept in diffused light to 18-8-36.	Exposed to sunlight to 19-9-36.	Kept in diffused light to 19-9-36.	Exposed to sunlight to 4-11-36.	Kept in diffused light to 4-11-36.
500 g. soil +100 g. cow-dung	NH₃-N =	0·004	0·0031	0·0026	0·0022	0·002	0·0021	0·0018
	NO₃-N =	0·0018	0·0035	0·0035	0·0024	0·0022	0·0028	0·0026
	Total N =	0·0905	0·100	0·100	0·1124	0·112	0·140	0·1324
500 g. soil +100 g. Cow-dung +5 g. Molasses	NH₃-N =	0·004	0·0028	0·0026	0·0021	0·0019	0·0018	0·0017
	NO₃-N =	0·0018	0·0043	0·0043	0·0022	0·0021	0·0026	0·0025
	Total N =	0·0905	0·100	0·100	0·1124	0·112	0·1386	0·1348
500 g. soil +100 g. Sawdust	NH₃-N =	0·0058	0·0017	0·0018	0·0016	0·0016	0·001	0·0008
	NO₃-N =	0·0021	0·0026	0·0023	0·0018	0·0018	0·0019	0·0019
	Total N =	0·083	0·0875	0·0822	0·0881	0·0881	0·0881	0·0882
500 g. soil +100 g. Sawdust +5 g. Molasses	NH₃-N =	0·0058	0·0014	0·0019	0·0012	0·0013	0·0014	0·0008
	NO₃-N =	0·0021	0·0025	0·0022	0·0018	0·0018	0·0018	0·0019
	Total N =	0·083	0·0875	0·0875	0·0881	0·0881	0·0888	0·0882

Field trials with cow-dung.

		Analysis just after mixing on 18-9-36.	Analysis on 16-10-36.	Analysis on 16-11-36.
25 tons of cow-dung per acre of soil.	NH₃-N =	0·0018	0·0025	0·0023
	NO₃-N =	0·0018	0·0016	0·0018
	Total N =	0·052	0·0608	0·081
25 tons of cow-dung +2·5 tons of molasses per acre of soil	NH₃-N =	0·0018	0·0023	0·0025
	NO₃-N =	0·0018	0·0015	0·0017
	Total N =	0·053	0·070	0·070

of ammonia after the addition of molasses and aeration increased three
to four times the amount originally present in the soil.   By the application
of 3600 kilograms of molasses per acre of land, and digging and watering the
soil once every 10 days for two months (May and June, 1935), 564 kilograms
of rice (*Aus*) grains and 1076 kilograms of straw were obtained by us in the
molassed land, while 340 kilograms of rice grains and 896 kilograms of straw
were grown in the control land.

Recent work of Sethi, Batham, and Nigam in the U.P. and of Mirchandani
in Behar (private communication) shows that molasses not only adds nitrogen
to the soil by fixation and improves the crop yield with wheat, rice and sugar-
cane but improves alkali soils as well.   These results are in entire confirmation
of the observations of Dhar and his collaborators.

TABLE 31.

Nitrogen fixation in the oxidation of sodium salts of organic acids.

	NH₃-N.	Nitric-N.	Total-N.	Total-C.	Heat of combustion of the acid per 1 gm.
		Analysed on 14-3-36			
Sodium tartrate 12·924 g.+200 g. soil ..	0·00186	0·00164	0·0458	2·268	
Sodium citrate 12·22 g.+200 g. soil ..	0·00186	0·00164	0·0458	2·424	
Sodium stearate 10·8 g.+200 g. soil ..	0·00186	0·00164	0·0458	4·384	
Sodium palmitate 10·7 g.+200 g. soil	0·00186	0·00164	0·0458	3·887	
Sodium oleate 10·86 g.+200 g. soil ..	0·00186	0·00164	0·0462	4·02	
		Analysed on 16-7-36.			
Sodium tartrate 12·924 g.+200 g. soil ..	0·0014	0·00144	0·0467	1·872	1·88 Cal.
Sodium citrate 12·22 g.+200 g. soil ..	0·0014	0·00144	0·05	1·91	2·48 Cal.
Sodium stearate 10·8 g.+200 g. soil ..	0·00116	0·00194	0·0583	2·323	. . . .
Sodium palmitate 10·7 g.+200 g. soil	0·0019	0·00268	0·054	2·212	9·21 Cal.
Sodium oleate 10·86 g.+200 g. soil ..	0·0014	0·0025	0·0534	2·4522	. . . .

The foregoing results show that cellulosic substances like filter paper,
dry leaf, etc., when mixed with soil and exposed to sunlight or kept in the dark,
cause nitrogen fixation.   When mixed with small amounts of molasses the
cellulosic substances undergo oxidation more readily and cause greater fixation
of atmospheric nitrogen.   The nitrogen fixation in sunlight is greater than
in the diffused light or in the dark.   Similar results have been obtained with
cow-dung and wood fibre.   These results are most important, because they

show that cellulosic materials, plant residues, leaves, cow-dung, etc. not only increase the humus content of the soil, and improve the soil tilth, moisture retention capacity, and act in the conservation of the soil nitrogen, but these substances also add nitrogen to the tropical soil by nitrogen fixation. Hence, cow-dung, which is used as a manure, has been found to supply to the soil not only the nitrogen it contains but it can also add nitrogen to the soil from the nitrogen of the air by fixation.

According to Mutterlein's calculation (Mutterlein, 1913) one acre of soil in Germany receives yearly about 200 kgms. of cellulose in the form of manure. It appears that this large amount of cellulosic matter added to the soil may be partially utilised in nitrogen fixation in temperate climates. In tropical climates, however, due to the high temperature and great intensity of sunlight and the greater activity of the *Azotobacter*, the soluble carbohydrates, pentosans and cellulosic substances are oxidised at the soil surface at a great speed with the liberation of large amounts of energy necessary for nitrogen fixation. Hence manuring of tropical soils by the addition of molasses and cellulosic materials is a highly important practical proposition. We are of the opinion that Indian soils would have been exhausted from the nitrogen point of view long ago had not the compensating agency, e.g. the fixation of atmospheric nitrogen by the addition of carbohydrates, pentosans and cellulosic materials to the soil, been counteracting the nitrogen loss. Moreover, the researches of Dhar and Atma Ram (1933) show that the tropical soil receives more available nitrogen from rain water than in temperate climates.

The results recorded in Table 31 show that nitrogen fixation also takes place when sodium salts of organic acids are allowed to oxidise in air on the soil surface. Our experimental results show that the greater the amount of energy liberated in the oxidation of the sodium salts of organic acids, the greater is the amount of nitrogen fixed. Thus with sodium stearate, palmitate, and oleate there is more nitrogen fixation than with the sodium salts of lower acids.

Russell ('Soil Conditions and Plant Growth', 1932, page 362) has reported that the nitrogen content of a grass land increased from 0.152% in 1856 to 0.338% in 1912. Similarly a land permanently covered with vegetation for 24 years showed an increase from 0.108% to 0.145%. It appears that this increase in the total nitrogen content of these soils is chiefly due to the fixation of nitrogen from the air caused by the liberation of energy from the oxidation of cellulosic and other carbonaceous substances on the surface of the soil.

INFLUENCE OF LIGHT ON NITRIFICATION AND AMMONIFICATION.

In publications from these Laboratories (Compare Dhar 'Influence of light on some Biochemical Processes'.—Society of Biological Chemists, Bangalore, India, 1935) we have tried to establish that light plays an important rôle in the processes of ammonification, nitrification, denitrification and nitrogen

fixation under aërobic conditions in the soil. From our experimental results we are convinced that all these soil processes can take place in the complete absence of micro-organisms provided light is available. It is gratifying to note that soil bacteriologists like Dr. Corbet, working at Jealott's Hill Experimental Station, England, Dr. Allen of the Hawaii University, and Messrs. Sarkaria and Fazaluddin of the Agricultural College, Lyallpur, Punjab, and others are in general agreement with our conclusions, although some investigators were unable to confirm our observations. The main difficulty of this type of work is that in all these processes, ultraviolet light being more effective than visible radiations, glass vessels are not much good as they cut off most of the ultraviolet radiations. When proper precaution is taken regarding the technique, our results ought to be easily reproducible.

Recently Wad and Aurangabadkar (1936) have obtained greater amounts of nitrate formation in sunlight than in the shade using sterile and ordinary soils in the nitrification of ammonium sulphate and composts, but these authors attribute without proper evidence the greater nitrification in sunlight to higher temperature rather than to sunlight. In this connection, the following statements of Corbet (1935 ; 1934) are of considerable interest :—' *The photochemical oxidation of ammonia to nitrous acid*. The recent investigations of Dhar and his co-workers show clearly that nitrite formation can be effected in the absence of micro-organisms. In the present research, experiments were carried out to determine the extent of the photochemical oxidation of ammonium sulphate and the results obtained by the Indian investigators were confirmed.

' The criticisms advanced by Fraps and Sterges against the work of Dhar and Gopala Rao are without substance, since in their experiments, soil was exposed to the sun in pyrex beakers covered with glass. The writer has confirmed that no ultraviolet radiations of wavelength capable of oxidising ammonium salts to nitrite can penetrate these materials.'

Moreover, O. N. Allen (1934) has made the following observations :—'*Photochemical nitrification* :—The work of Rao and Dhar has done much to explain nitrification in tropical areas upon a purely chemical basis. Their results seem to warrant that to a certain extent nitrification is photochemical in nature, the process taking place at the surface of various tropical soils in the presence of certain photosensitisers under the influence of sunlight.'

TABLE 32.

Nitrification of Ammonium salts exposed to sunlight for 550 hours.

Condition		Nature of soil	Amount of salt unoxidised	Amount of salt oxidised	Percentage oxidised
			NH$_4$Cl.		
Sunlight	..	unsterilised	1·98 gm.	2·6 gm.	58
Dark	..	,,	4·2	0·7	14
Sunlight	..	sterilised	2·3	2·3	50
Dark	..	,,	4·4	0·5	10·2
			(NH$_4$)$_2$HPO$_4$		
Sunlight	..	unsterilised	1·85 gm.	2·8	60·2
Dark	..	,,	4·4	0·55	11·1
Sunlight	..	sterilised	2·15	2·75	55
Dark	..	,,	4·6	0·30	6
			(NH$_4$)$_2$SO$_4$		
Sunlight	..	unsterilised	3·35 gm.	1·15	23
Dark	..	,,	4·75	0·15	3
Sunlight	..	sterilised	4·2	0·8	16
Dark	..	,,	4·85	0·1	2

Influence of light on Ammonification.

In a recent communication Dhar and Atma Ram (1933) have shown that aqueous solutions of amino acids like glycine are very readily oxidised into ammonia, formaldehyde and carbon dioxide when exposed to air and light. Experiments carried on *in vitro* by Dhar and Mukerji and Gopala Rao and Dhar show that the amounts of ammonia obtained on exposing solutions of amino acids like glutamic acid, aspartic acid, etc. to light increase on passing air through solutions of these amino acids. These are cases of oxidative deamination. The formation of ammonia from these amino acids is greatly increased by the presence of the solid surfaces like TiO$_2$, ZnO, SiO$_2$, etc., the best results are obtained with TiO$_2$. The following Table shows the amounts oxidized with different nitrogenous substances after 20 hours' exposure to sunlight. In the dark, there is no oxidation.

TABLE 33.

		No surface		With 5 gms. TiO$_2$	
		Air not passed (percentage oxidised)	Air passed (percentage oxidised)	Air not passed (percentage oxidised)	Air passed (percentage oxidised)
Aspartic acid	..	0·062	0·064	4·43	5·32
Glutamic acid	..	0·059	0·063	0·35	0·44
Egg-yellow	..	0·16	0·194	5·7	9·7
Egg-white	..	0·145	0·222	17·6	40·
Blood serum	..	0·844	0·996	10·8	12·8
Gelatine	..	0·762	0·822	39·9	45·1

TABLE 34.

The following results show that proteins are more easily oxidised than the amino acids :—

	Percentage oxidation after 20 hours' exposure with TiO_2	Amount of total nitrogen in grams as NH_3 per litre
Glutamic acid	0·34	0·570
Aspartic acid	4·45	0·640
Gelatine	39·9	2·377
Blood serum	10·8	4·715
Egg-white	17·6	3·180
Egg-yellow	5·7	3·505

These experimental results show that on exposing ammonium salts to light mixed with soil the greater part of the ammonium compound is oxidised to nitrite and nitrate after 550 hours' exposure with ammonium phosphate and chloride. The sulphate is much less oxidised. The oxidation in vessels coated with black Japan enamel (dark) is much smaller than those receiving light. If nitrification is mainly a bacterial process as is generally believed, the amount of nitrification in the vessels in the dark with unsterilised soil should not have been materially different from those exposed to light. Moreover, the nitrification in the vessels kept in the dark and containing unsterile soil is not widely different from those with the sterile soil. It seems likely that due to the high temperature also prevailing in the dark vessels, the bacteria considerably decrease in numbers. As the light and dark experiments are exactly comparable, any bacterial contamination due to the introduction of air containing dust particles would affect the nitrification in all sets equally, because the experiments are conducted at the same place. The results of our experiments, however, show that nitrification is only prominent in vessels receiving sunlight and this is not likely to be a matter of chance only. Exactly similar behaviour is observed in our experiments on ammonification.

In a recent quantitative study we have been able to show that dilute solutions of sodium or potassium nitrite are almost completely oxidised to nitrate when exposed to light along with photocatalysts like TiO_2, ZnO, Fe_2O_3 and sterilised soil in the absence of bacteria. In the following table the results obtained with ZnO as the photocatalyst are summarized :—

TABLE 35.

Photo-oxidation of nitrite to nitrate.

Amount of nitrite-nitrogen and total N in gm./100 c.c. after an exposure of—

Original amount to start with		20 hours		40 hours		60 hours		80 hours	
NO_2-N	Total N	NO_2-N	Total N	NO_2-N	Total N	NO_2-N	Total N	NO_2-N	Total N
0·0686	0·0686	0·0648	0·0684	0·06034	0·0684	0·050	0·0684	0·0432	0·0684
0·0343	0·0343	0·0280	0·03452	0·0234	0·03398	0·01522	0·03396	0·00761	0·0341
0·0171	0·0171	0·00934	0·01646	0·003226	0·01599	0·00006	0·01598	*nil*	0·0162
0·00855	0·00855	0·00108	0·00848	*nil*	0·00848	*nil*	0·00848	*nil*	0·00848

The foregoing results show that in the more concentrated solutions the amount of oxidation is less, but in the dilute solutions even after 40 hours' exposure the oxidation of the sodium nitrite to sodium nitrate is complete. It is clear, therefore, that aqueous solutions of a nitrite when exposed to light and air undergo the following reversible change :—

$$2NaNO_2 + O_2 \rightleftharpoons 2NaNO_3$$
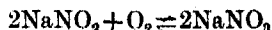
Thus from the experimental work carried on in these laboratories we find that not only are ammonium salts oxidised to nitrite by air in the presence of light, but the nitrites are also in their turn readily converted into nitrate when exposed to light and air along with the photocatalyst. It seems, therefore, that the whole processes of nitrification and nitrogen-fixation may be photo-chemical.

The increase in the fertility of soil as a result of exposure to sunlight as practised in India, Egypt and other countries from time immemorial can be easily explained from our photochemical theory.

Influence of temperature on bacterial nitrification.

The bacterial theory of nitrification and of other soil processes have been holding the field to a large extent. However, there are certain facts known to us which do not find a solution on the bacterial theory. Our attention was, therefore, directed to find out the cause of these divergencies and various experiments are being conducted in these laboratories.

We made a study of the effects of temperature on nitrite formers and *Azotobacter* in pure cultures. Bacterial decomposition of urea was also studied by us. We further investigated the oxidation of nitrites to nitrates in sunlight in presence of photocatalysts like ZnO, TiO_2, Fe_2O_3, soil, etc. We shall briefly summarise our results and the conclusions arrived at.

Influence of temperature on bacterial nitrication.

For the study of nitrite formers, a pure culture of nitrite forming bacteria was prepared from the garden soil by Omeliansky's method of elective culture, the medium employed being :—

Ammonium Sulphate	..	..	..	2 to 2·5 gm.
Potassium Phosphate	..	..	..	1 ,,
Magnesium Sulphate	..	..	..	0·5 ,,
Sodium Chloride	..	..	..	2 ,,
Ferrous Sulphate	..	..	..	0·4 ,,
Distilled Water	..	..	..	1000 c.c.
Magnesium Carbonate	..	..	..	.. Excess

(0·5 gm. per 50 c.c. of the medium)

Equal portions of the medium containing a known amount of the culture were taken in conical Jena-glass flasks and were kept at various temperatures. The amount of nitrite formed was estimated by a Duboscq colorimeter from time to time using a mixture of 0·8 per cent solution of sulphanilic acid in acetic acid of specific gravity 1·04 and 0·5 per cent solution of naphthylamine in acetic acid of the same specific gravity as the indicator.   The results are recorded below :—

TABLE 36.

Amount of nitrite formed at various temperatures (Gm. of NO_2 per litre).

Time	Nitrite formed at temperatures of						
	0°	15°	20°	25°	30°·	35°	40°
Hours.							
67	0·000253	0·0001525	0·001169	0·005066	0·00792	0·008848	0·00064
115	0·000281	0·0002884	0·00175	0·008505	0·02304	0·0438	0·000689
163	0·000281	0·0004045	0·002779	0·01777	0·0497	0·09385	0·000844
187	0·000281	0·0006595	0·002953	0·02656	0·0673	0·1438	0·000950
211	0·000281	0·001318	0·00376	0·0386	0·08503	0·1987	0·001076
235	0·000281	0·002163	0·004468	0·05797	0·1026	0·2715	0·00141
259	0·000281	....	0·00559	0·08585	0·12595	0·3585	0·001781

At 50° the amounts of nitrite formed in the flasks containing the bacteria were the same as in the control flasks containing no bacteria.

The results recorded in Table 36 clearly show that the optimum temperature of nitrification with the tropical nitrite forming bacteria is about 35°.   The optimum temperature in colder countries is near about 25°.   On account of the high temperatures existing for the greater part of the year in the tropics the bacteria in soils of tropical countries have so adapted themselves as to

thrive best at 35°. It is interesting to note that Panganiban (1925) working in the Philippines has also observed an optimum temperature of 35° with his nitrite-forming bacteria.

Table 36 shows that at 0° the bacteria are capable of maintaining the life activity for some days but a prolonged exposure to this temperature ultimately results in the complete stoppage of their life activity. Such a culture when brought back again to optimum conditions fails to show any further sign of growth even after being kept for 9 months. At 50° also we find that the bacteria are incapable of existence.

The study of the bacterial ammonification of urea at different temperatures gave the following results :—

Influence of temperature on the ammonification of urea.

TABLE 37.

Amounts in 5 c.c. of the urea solution which was equivalent to 0·0444 gm. N.

Temperature	31°.		35°		40°		50°		55°	
Time in hours	NH₃-N in gms.	% ammonification	NH₃-N in gms.	% ammonification	NH₃-N in gms.	% ammonification	NH₃-N in gms.	% ammonification	NH₃-N in gms.	% ammonification
36	0·00195	4·39	0·007613	17·14	0·01628	36.66	0·00005	0·10	0·00004	0·09
60	0·01473	33·18	0·0225	50·7	0·02433	54·8	0·00006	0·11	0·00004	0·09
84	0·02347	52·9	0·0322	72·56	0·03246	73·1	0·000067	0·12	....	....
108	0·02442	55·0	0·03466	78·1	0·03495	78·7	....	....	....	....
132	....	....	0·0374	84·3	0·0379	85·4	....	....	....	....

The above results show that the optimum temperature for bacterial ammonification in the tropics is near about 40°. The maximum temperature for the survival of the bacteria seems to be between 50° and 55°.

Thus we see that the optimum temperature for ammonification is higher than the optimum for nitrification. This shows that ammonifying bacteria have a greater resisting capacity with respect to temperature than is the case with the nitrite-forming bacteria. A similar relationship has also been noticed by workers in colder countries though there the optima for nitrification and ammonification are much below those existing in the tropics.

Influence of temperature on nitrogen-fixation by Azotobacter.

The following procedure was adopted for the study of nitrogen-fixation by *Azotobacter* kept at various temperatures.

A three-days-old culture of *Azotobacter* cells was prepared and 0·2 c.c. of this was added to each flask containing forty cubic centimeter portions

of the sterile mannite medium plugged with absorbent cotton. The flasks were kept at various temperatures along with the control ones and the nitrogen fixed in the form of NH_3 was estimated from time to time by Nessler's reagent in a Duboscq colorimeter.   The results are recorded below :—

TABLE 38.

Gram of ammoniacal N per litre.

Hours	At temperatures of							
	10°	20°	30°	35°	40°	50°	60°	70°
96	nil	0·00086	0·00105	0·00243	0·00096	0·000782	nil	nil
168	,,	0·002169	0·00677	0·0161	0·002749	0·001674	,,	,,
216	,,	0·00565	0·0116	0·0254	0·0064	0·00357	,,	,,
264	,,	0·00862	0·012	0·0296	0·00924	0·00535	,,	,,
312	,,	0·01041	0·015	0·0354	0·01054	0·00654	,,	,,
360	,,	0·01352	0·0167	0·0423	0·01375	0·00895	,,	,,
408	,,	0·0152	0·0207	0·0504	0·0153	0·0094	,,	,,

The foregoing results show that the maximum amount of nitrogen-fixation by *Azotobacter* which we isolated from our garden soil is at about 35° whilst at 10°, 60°, and 70° there is no nitrogen-fixation.   The cultures at 10° and 60° were plated on solid agar medium and it was found that a few colonies developed on the plates containing the culture at 10°, while on the plates containing the culture kept at 60° practically no colony appeared.   This shows that although a few *Azotobacter* cells may remain alive at 10° their activity is practically nil, which is evident from the fact that no ammonia formation could be detected in the experimental flasks kept at the said temperature.

Investigations carried on in different temperate countries show that the optimum temperature is appreciably lower for *Azotobacter* in colder countries than 35°.

In the summers of 1933 and 1936 we recorded the soil temperatures at Allahabad ; in the month of April it rose to 50° at 2 inches depth.   May and June of 1933 were frequently cloudy and the summer was a mild one.

Leather, working at Pusa, India, stated that the maximum temperature at Pusa may rise to 70° at the soil surface and 60° at a depth of 1 or 2 inches.   In Egypt the recorded temperature is 65° at the surface and 56° at a depth of 2 inches.   From our measurements on the influence of temperature on bacterial nitrogen transformations we find that 35° is generally the optimum temperature for these processes in the tropics.   Beyond 50° the bacterial effect becomes negligible.   Hence, in the tropics, nitrification and nitrogen-fixation in soil can not be to any large extent of bacterial origin in the months of April, May, June and July in the daytime when the soil temperature is much greater

than the optimum for these bacteria. In these very months the nitrate in the soil is, however, the greatest. Even in colder countries like England and Germany, the soil temperature may rise to 35° or more in summer, although the optimum temperature for bacterial nitrification there is stated to be 25°.

In these countries also the bacterial nitrification must be greatly reduced in the summer months as a result of the soil temperature becoming greater than the optimum temperature for bacterial nitrification, though the nitrate content of the soil in these countries is also largest in the summer time.

It is generally agreed that nitrification is most active at the surface of the soil. According to Prescott and Piper nearly 80% of the nitrate accumulation takes place in the first $3\frac{1}{2}$ inches of the soil from the surface. The observations recorded previously show that the soil temperature in the summer months in tropical countries must not be much below 50° even at the depth of $3\frac{1}{2}$ inches from the surface, although the bacterial nitrification has the optimum temperature of 35°. It appears, therefore, that in the first $3\frac{1}{2}$ inches of the soil, where there is maximum nitrification as observed by different investigators, very few bacteria can exist in tropical countries in summer months, although the amount of nitrate in the soil is maximum in summer. We are led to conclude, therefore, that agencies other than bacterial must be active in causing nitrification which is going on at a maximum speed in the soil in summer months within $3\frac{1}{2}$ inches of the soil. As we have observed that light markedly accelerates the oxidation of amino acids to ammonia, of ammonium salts to nitrites, of nitrites to nitrates and the fixation of atmospheric nitrogen, and that all these oxidations are accelerated by increase of temperature, we are led to believe that light absorption and increase of temperature play a more important rôle than bacteria in nitrogen changes in soil in the summer months.

In publications from these laboratories it has been shown that the oxidation of ammonium salts mixed with sterilised or unsterilised soil in covered vessels coated with Japan black enamel, when kept in the sun along with the vessels receiving light, is much smaller than in those exposed to light. If nitrification were mainly a bacterial process the amount of nitrification in the vessels in the dark with the unsterilised soil should not have been materially different from those exposed to light. We have made numerous comparative experiments like those on the oxidation of ammonium salts to nitrite and of nitrite to nitrate with both sterilised and unsterilised soil kept in light and in the dark and we find that the formation of nitrite and nitrate is always much greater in the vessels exposed to light than in those kept in the dark.

From all the points discussed in the preceding sections it seems that nitrogen transformations in soil are due more to light than to bacteria specially in tropical countries.

AVAILABLE NITROGEN IN TROPICAL SOILS.

Regarding the amounts of available nitrogen (sum of ammoniacal and nitric nitrogen) present in English soils, Russell (1932) has stated as follows :—

'In normal conditions, the nitrate and ammonia together rarely account for more than one per cent of the nitrogen in the soil.'

'Usually the total amount of nitrogen is so large in comparison with the amount of nitrate that the changes in amount fall within the limits of experimental error.'

'Neither ammonia nor nitrate normally occurs in the soil in any great quantity ; an usual range on land carrying vegetation is from 5 to 25 parts of nitric nitrogen and about 5 to 10 parts of ammonia per million of soil, corresponding to about one to three per cent of the total nitrogen.'

The amount of available nitrogen in Russian soils varies from 0·36 to 4·6%.

It has already been emphasised that the oxidation processes taking place in the soil are facilitated to a greater extent in tropical countries due to sunlight and higher soil temperatures than in temperate climates. It is expected, therefore, that the percentage of available nitrogen in the tropical soil is greater than in cold countries.

In order to test this point, we have determined the total, ammoniacal and nitric nitrogen of samples of soils collected from different parts of India. Our results can be summarised as follows :—

ASSAM (Nyagogra tea estate). Four samples of soil analysed ; the available nitrogen varies from 25·1 to 40·4% of the total nitrogen, of which the variation is from 0·092 to 0·139% of the soil.

BENGAL (Dacca and Nadia). Six samples analysed ; the available nitrogen varies from 14·3 to 29·7% of the total nitrogen, of which the variation is from 0·057 to 0·227% of the soil.

BIHAR (Pusa). Five samples collected in July, 1932 and analysed in April, 1935 ; the available nitrogen varies from 28·1 to 47·7% of the total nitrogen, of which the variation is from 0·0238 to 0·0313% of the soil.

UNITED PROVINCES (Allahabad). (a) Thirteen samples of ordinary garden soil analysed ; the available nitrogen varies from 10 to 31·6% of the total nitrogen, of which the variation is from 0·0347 to 0·0582% of the soil.

(b) Five samples of molassed soil of which the C : N ratio is constant, analysed ; the available nitrogen varies from 11·7 to 28% of the total nitrogen, of which the variation is from 0·0437 to 0·09% of the soil.

THE PUNJAB (Ranjitkot, Hiyatpur and Chhanwali). Three samples analysed ; the available nitrogen varies from 13·4 to 15·2% of the total nitrogen, of which the variation is from 0·04 to 0·0582% of the soil.

MADRAS (Waltair). Two samples analysed ; the available nitrogen varies from 15 to 24·9% of the total nitrogen, of which the variation is 0·0309 to 0·0625% of the soil.

The foregoing results show that the amounts of available nitrogen varies from 10 to 47·7% of the total nitrogen in the soils collected from different parts of India. The percentage of available nitrogen of a soil from Bangalore, which is a cool place, is 8·5. Hence the portion of available nitrogen in comparison with the total nitrogen in tropical soils is much greater than that

present in soils of temperate climates. It appears, therefore, that the solar radiations, which fall on the tropical soil, help in the oxidation of the nitrogenous substances present in the soil, which is rendered suitable for plant growth, although the total nitrogen in tropical soils is generally less than in those of temperate countries.

Significance of carbon-nitrogen ratio in soil.

It is well known that in soil which is well-aerated, the chemical changes affecting the carbon and the nitrogen present in the soil are intimately connected. It is generally believed that the combined nitrogen existing in the soil can form nitrate only if the ratio of carbon to nitrogen is not greater than 10 to 11; when the proportion of carbon is greater, the excess is oxidised to carbon dioxide and the nitrogen remains as complex protein. When, on the other hand, the proportion of nitrogen is greater than the above ratio, the nitrogenous compound is changed into ammonia and nitrate.

From our researches on the nitrogen transformations in the soil, we are of the opinion that when the carbon content of the soil is increased by the addition of energy-rich substances like carbohydrates, cellulose, etc. the energy-rich substances are readily oxidised on the soil surface causing nitrogen fixation. This important factor tends to increase the nitrogen content of the soil. The oxidation of carbohydrates, cellulosic materials, etc. on the soil surface may take place through the agencies of bacteria, sunlight, inductors, and catalysts. Whatever may be the agency which is effective, these processes cause liberation of energy which is utilised in the nitrogen-fixation. Under ordinary soil conditions, all these agencies are responsible for the oxidation of carbohydrates and cellulosic materials, and in this process the soil is enriched from the nitrogen point of view. In presence of large amounts of carbohydrates and cellulosic materials, the proteins, amino acids and ammonium salts present in soil are protected from oxidation and these are conserved in the soil. When the carbonaceous substances are oxidised to a great extent, ammonification, nitrification, etc., which are also mainly oxidation processes accelerated by sunlight, high temperature, surface of catalysts, inductors, bacteria, etc., become prominent in the soil. In these processes appreciable amounts of loss of nitrogen in the gaseous state takes place.

The retarding influence of different carbohydrates and carbonaceous compounds in the processes of ammonification and nitrification is observed with different bacteria, fungi, etc. of different energy and food requirements, and is not regulated by their demands, but forms a part of an universal phenomenon taking place in the animal, plant, and in soil processes as well as in vitro, in which it is always observed that a readily oxidisable organic substance can act as a negative catalyst in the oxidation of another substance. We are of opinion, therefore, that the carbon-nitrogen ratio in soils is not controlled by the energy requirements of the micro-organisms, as advocated by Doryland

(1916) but is regulated by the ease with which proteins, amino acids, ammonium salts, etc. are oxidised by air, aided by bacteria, catalysts and light in presence of carbonaceous substances under different conditions and the oxidations taking place in the soil seem to be guided by the same laws, which rule animal metabolism.

Influence of temperature on the carbon-nitrogen ratio in soils.

A garden soil was heated in a steam oven at 80°–85° for nearly 18 months and the carbon-nitrogen ratio was determined from time to time. The following results show that the carbon-nitrogen ratio appreciably increases as the heating is continued :—

TABLE 39.

Date of analysis			Carbon	Nitrogen	C/N
23-2-35	..	..	0·563	0·056	10·05
23-3-35	..	..	0·57	0·0544	10·45
23-4-35	..	..	0·5608	0·0509	11·01
23-7-35	..	..	0·5646	0·045518	12·48
4-5-36	..	..	0·5581	0·04227	13·2

The foregoing results support our contention that the greater the temperature of the soil, the higher is the carbon-nitrogen ratio.

Our experimental results show that the carbon-nitrogen ratio is highest in the soils from the Punjab and the value is 14·4 ; in the United Provinces it is 11·3, in Bihar it is 9·2 and in Bengal the ratio is 9·1. The carbon-nitrogen ratio in soils collected from different countries seem to support the above view-point. The average ratio of 50 English soils is 10. In Wales it is 9·2. In the Washington State after long cultivation the value is 10·2. In the Sudan it is 12·6 and in Transvaal it is 14·4.

NITROGEN LOSS FROM SOIL IN SUNLIGHT AND ITS RETARDATION.

The researches of Lipman and Blair, *Soil Sci.*, *12*, 1 (1921), Russell and Richards, *J. Agric. Sci.*, *8*, 495 (1917), Shutt, *ibid.*, *3*, 335 (1910) and others show that nitrogen in the gaseous stage is lost from soils when the conditions are favourable for oxidation. The loss of nitrogen in this process may be more than double the amount of nitrogen taken up by the plant grown on the soil. Nearly 70% of the added nitrogen is said to have been lost when wheat plots in Rothamsted, England, have received 14 tons of farmyard manure containing 200 lbs. nitrogen per acre.

A greater loss of nitrogen is observed when a manure is composted under aerobic than anaerobic conditions. According to Niklewski, *Rocz. Nauk. Roln.*, *9*, 1 (1923), there is more loss of nitrogen from stable manure in presence of nitrifying bacteria than in their absence. It has also been reported that in the nitrification of different oil-cakes, the loss of nitrogen is the greatest with the most easily and quickly nitrifiable cakes. Recently Viswanath,

Sci. Reports Dept. Agric. Madras (1930-31) has obtained greater nitrogen loss and greater velocity of oxidation in the nitrification of ammonium salts than with farmyard or green manure. It is established that when there is a large amount of carbonaceous matter present in the manures along with nitrogenous compounds, the velocity of the oxidation of nitrogenous compounds and the amount of nitrogen loss are also decreased.

Experiments carried on at different places show that the total amount of nitrate present in soils containing crops is less than that in neighbouring fallow soils even when a correction is applied for the amount of nitrate taken up by the crop. The oxidation processes are more vigorous in soils with crops than in those without them. Russell (Soil Conditions and Plant Growth, pp. 368-369 ; 1932) has stated this problem of the loss of nitrogen in the following words :—' There is considerable difficulty in accounting for the nitrogen lost from the soil during the first 20 or 30 years of cultivation. It has, therefore, been supposed that nitrogen is evolved during the oxidation, and as all attempts to break off nitrogen from nitrate in these conditions have failed, it is assumed to come from the organic matter. This assumption involved the difficulty that no loss of nitrogen has been observed in the straightforward bacterial oxidation of organic substances such as albumin, asparagin or mixtures such as urine or fæces.' ' Yet somehow and somewhere gaseous nitrogen must be evolved to balance the considerable amount of fixation that is known to take place.'

The results obtained by Dhar, Tandon, and Mukerji, *J. Indian Chem. Soc.*, *12*, 67 (1935) show that the loss of nitrogen on exposing ammonium salt solutions to light and air is always greater in light than in the dark. The oxidation of ammonium salts by air is greater in light than in the dark and hence the possibility of the formation of ammonium nitrite is greater in light than in the dark. Several years ago Dhar, *Proc. K. Akad. Wet. Amsterdam*, *23*, 308 (1920) observed that solutions of ammonium nitrite decompose into nitrogen and water when exposed to sunlight and this photochemical decomposition is facilitated by acids and different solid surfaces. Moreover, the recent observations of Dhar, Tandon, and Mukerji (*loc. cit.*) show that solutions of ammonium chloride and sodium nitrite decompose readily with evolution of nitrogen when exposed to sunlight in glass beakers or quartz tubes mixed with sterilised or unsterilised soil. This decomposition can take place under completely sterilised conditions in the complete absence of bacteria. Moreover, this decomposition is less pronounced in dilute solutions of ammonium nitrite and also when cane sugar is added to the solution containing ammonium and nitrite ions.

All these observations have been explained from the viewpoint that in the processes of ammonification and nitrification taking place in the soil or in solutions, ammonium nitrite is produced. Solutions of ammonium nitrite have been found to decompose into nitrogen and water readily by increase of temperature or exposing them to light. The formation of ammonium

nitrite from ammonium salts or proteins requires oxygen and that is why this type of denitrification is facilitated by increased soil aeration, and also soil acidity, as nitrous acid also undergoes decomposition according to the equation :

$$3\,HNO_2 \rightleftharpoons HNO_3 + 2\,NO + H_2O.$$
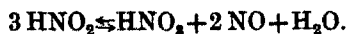
This chemical change is also markedly accelerated by light.

There is also the possibility of the reaction of nitrous acid on amines, amides and amino acids, which may sometimes be formed in the decomposition of soil organic substances. This important phenomenon first studied systematically by Lipman and Blair and emphasised by Russell has now been satisfactorily explained by Dhar and collaborators, *Nature*, *134*, 572 (1934).

Addition of carbonaceous substances like molasses tends to preserve the nitrogenous compounds present in the soil by decreasing the probability of the formation and decomposition of ammonium nitrite.

TABLE 40.

Decomposition of ammonium nitrite solutions at 20° and 30°.

NH_3-N added as $(NH_4)_2SO_4 = 0.14$ g. = 10 cc. NO_2-N added as $Ba(NO_2)_2 = 0.148$ gr. = 10 cc. Total-N added = 0.29 gr.

Light (1000 watt tungsten filament lamp).

Exposure at		NH_3-N. left.	NO_2-N. left.	Total-N. left.	NH_3-N. lost.	NO_2-N. lost.	Total-N. lost.	% lost.
30° for 5 hours	..	0·1343 g.	0·1422 g.	0·2786 g.	0·0057 g.	0·0058 g.	0·0114 g.	3·9
30° for 10 hours	..	0·1272	0·135	0·2642	0·0128	0·013	0·0258	8·2
30° for 20 hours	..	0·112	0·12	0·234	0·028	0·028	0·056	19·6
20° for 5 hours	..	0·14	0·148	0·29	*nil*	*nil*	*nil*	*nil*
20° for 10 hours	..	0·1312	0·14	0·271	0·0088	0·0098	0·019	6·5
20° for 20 hours	..	0·123	0·132	0·257	0·017	0·016	0·033	11·3
20° for 40 hours	..	0·1152	0·1248	0·2402	0·0248	0·0232	0·0498	17

Dark.

		NH_3-N. left.	NO_2-N. left.	Total-N. left.	NH_3-N. lost.	NO_2-N. lost.	Total-N. lost.	% lost.
30° for 5 hours	..	0·14	0·148	0·29	*nil*	*nil*	*nil*	*nil*
30° for 10 hours	..	0·1372	0·1452	0·2855	0·0028	0·0027	0·0045	0·1
30° for 20 hours	..	0·1327	0·14	0·2754	0·0073	0·008	0·0146	5
20° for 5 hours	..	0·14	0·148	0·29	*nil*	*nil*	*nil*	*nil*
20° for 10 hours	..	0·14	0·148	0·29	*nil*	*nil*	*nil*	*nil*
20° for 20 hours	..	0·14	0·148	0·29	*nil*	*nil*	*nil*	*nil*
20° for 40 hours	..	0·1318	0·14	0·2729	0·0082	0·008	0·0171	5·7

		Loss of nitrogen in			Percentage loss in	
		Dark + Light.	Dark only.	Light only.	Dark.	Light.
5 hrs. at 30°	..	0·0114 g.	*nil*	0·0114 g.	*nil*	3·9
10 hrs. at 30°	..	0·0258	0·0045	0·0213	0·1	8·1
20 hrs. at 30°	..	0·056	0·0146	0·0414	5·0	14·6
5 hrs. at 20°	..	*nil*	*nil*	*nil*	*nil*	*nil*
10 hrs. at 20°	..	0·019	*nil*	0·019	*nil*	6·5
20 hrs. at 20°	..	0·033	*nil*	0·033	*nil*	11·3
40 hrs. at 20°	..	0·0498	0·0171	0·0327	5·7	11·5

The foregoing results show that solutions of ammonium nitrite decompose appreciably in the dark at 20° and 30°. This decomposition is appreciably increased by exposing the solutions to the total light from a 1000 watt tungsten filament lamp.

TABLE 41.

Influence of sunlight on the nitrification and denitrification of ammonium sulphate added to fields.

138·6 kg. of nitrogen as $(NH_4)_2SO_4$ per acre of land used.

Condition.		NH_3-N.	Nitric-N.	Available-N.	Total-N.	Total-C.	Date of Analysis.
Uncovered	..	0·032%	0·0028%	0·0348%	0·14%	0·476%	18-1-36
Covered	..	0·0373	0·004	0·0413	0·148	0·48	,,
Uncovered	..	0·008	0·00934	0·01734	0·1081	0·481	30-1-36
Covered	..	0·032	0·0056	0·0376	0·1382	0·482	,,
Uncovered	..	0·00582	0·01132	0·01714	0·1032	0·478	19-2-36
Covered	..	0·0224	0·0082	0·0306	0·1328	0·478	,,
Uncovered	..	0·00504	0·01194	0·01698	0·0995	0·478	9-3-36
Covered	..	0·02176	0·00924	0·031	0·1324	0·472	,,
Uncovered	..	0·00416	0·01224	0·0164	0·0982	0·478	4-4-36
Covered	..	0·0211	0·00976	0·0308	0·1312	0·478	,,
Uncovered	..	0·00324	0·01302	0·1626	0·09212	0·478	25-4-36
Covered	..	0·0185	0·01144	0·0299	0·1308	0·478	,,

TABLE 42.

277·2 kg. of nitrogen as $(NH_4)_2SO_4$ per acre of land used.

Condition.		NH_3-N.	Nitric-N.	Available-N.	Total-N.	Total-C.	Date of Analysis.
Uncovered	..	0·0468%	0·0028%	0·0496%	0·200%	0·476%	18-1-36
Covered	..	0·0624	0·004	0·0664	0·2	0·482	,,
Uncovered	..	0·0234	0·01468	0·03808	0·167	0·481	30-1-36
Covered	..	0·0500	0·0048	0·0548	0·1902	0·482	,,
Uncovered	..	0·020	0·01488	0·03488	0·1425	0·478	19-2-36
Covered	..	0·0442	0·00844	0·05264	0·1842	0·478	,,
Uncovered	..	0·01844	0·01544	0·03388	0·1325	0·478	9-3-36
Covered	..	0·0425	0·00936	0·05186	0·1841	0·478	,,
Uncovered	..	0·01784	0·0157	0·03354	0·1281	0·472	4-4-36
Covered	..	0·04024	0·01056	0·0508	0·1834	0·478	,,
Uncovered	..	0·00862	0·01848	0·0271	0·1122	0·472	25-4-36
Covered	..	0·03824	0·01242	0·0506	0·1832	0·472	..

These experimental results show definitely that the nitrification of ammonium sulphate is much quicker in the plots receiving sunshine than in those which are covered with wooden planks. Moreover, in the uncovered plots there is more nitrogen loss than in the covered plots. Thus, when 138·6 kg. of nitrogen were added to the soil, the loss in nitrogen in the uncovered plots amounted to 34·2% in about 3 months, whereas in the covered plots the loss is only 11·6%. Similarly with 277·2 kg. of nitrogen the loss is 43·9% in the uncovered and 8·2% in the covered plot. These results conclusively prove that in presence of sunlight ammonium sulphate is nitrified

at a much greater speed than in the dark. Along with the greater velocity of nitrification in sunlight, there is a concomitant greater loss of nitrogen in sunlight than in the dark. These results strongly support our conclusion, that sunlight plays an important part in the nitrification and in denitrification in tropical countries.

We have already emphasised that this type of denitrification, when the conditions are favourable for oxidation and nitrification of the nitrogenous compounds in the soil, is caused by the formation and decomposition of NH_4NO_2 in the process of nitrification. The formation of ammonium nitrite from ammonium salts and proteins requires oxygen, and that is why this type of denitrification is facilitated by increased soil aeration. In the process of nitrification, the ammonium ion is replaced first, by the acidic NO_2 ion and finally by NO_3, and hence in the process of nitrification the acidity of the system increases. It is well known that the nitrous acid decomposes according to the equation

$$3\,HNO_2 \rightleftharpoons HNO_3 + 2\,NO + H_2O.$$

Moreover, the acids have been found to facilitate the thermal and photochemical decomposition of ammonium nitrite, which is temporarily formed in the soil in the process of nitrification. Murty and Dhar (1931) have also shown that sunlight or artificial light markedly accelerates the decomposition of nitrous acid according to the above equation. All these factors are responsible for the nitrogen loss from soils, when ammonium salts or proteins added or present in the soil undergo nitrification. In the previous pages it has been emphasised that the presence of carbonaceous substances like carbohydrates, fats, etc. along with the nitrogenous substances retard the nitrogen loss from soils. It has been shown by us that in presence of the carbonaceous substances, the velocity of nitrification of nitrogenous compounds is decreased and consequently the nitrogen loss is concomitantly decreased. The following field trials obtained with the addition of $(NH_4)_2SO_4$ to the soil with or without molasses show definitely that molasses retards the velocity of nitrification and denitrification in soils.

TABLE 43.

Retardation of nitrogen loss from field soils by the addition of molasses.

17·325 kgm. of nitrogen as $(NH_4)_2SO_4$ per acre of land used and 3000 kilograms of molasses per acre.

Condition.		NH₃-N.	Nitric-N.	Available-N.	Total-N.	Total-C.	Date of analysis.
Unmolassed	..	0·00832%	0·00350%	0·01182%	0·0583%	0·416%	27-9-35
Molassed	..	0·00814	0·00350	0·01164	0·0588	0·587	,,
Unmolassed	..	0·00636	0·00556	0·01192	0·0583	0·416	12-10-35
Molassed	..	0·00778	0·00426	0·01204	0·0609	0·578	,,
Unmolassed	..	0·00608	0·006	0·01208	0·0538	0·416	24-10-35
Molassed	..	0·00778	0·00582	0·01360	0·0625	0·501	,,
Unmolassed	..	0·00438	0·00714	0·01152	0·0538	0·411	7-11-35
Molassed	..	0·0070	0·00636	0·01336	0·0636	0·498	,,

TABLE 43—contd.

Condition.		NH$_3$-N.	Nitric-N.	Available-N.	Total-N.	Total-C.	Date of analysis.
Unmolassed	..	0·0042	0·00714	0·01130	0·0538	0·412	13-12-35
Molassed	..	0·0064	0·0064	0·0128	0·0634	0·500	,,
Unmolassed	..	..	..	..	0·0532	0·422	10-1-36
Molassed	..	0·0064	0·0064	0·0128	0·0638	0·489	,,
Unmolassed	..	0·00424	0·007	0·01124	0·0532	0·422	11-3-36
Molassed	..	0·00622	0·0066	0·01282	0·06349	0·4899	,,
Unmolassed	..	0·0042	0·007	0·0112	0·0532	0·434	30-4-36
Molassed	..	0·006	0·0066	0·0126	0·0635	0·489	,,

TABLE 44.

34·65 kg. of nitrogen as (NH$_4$)$_2$SO$_4$ per acre of land used and 3000 kilograms of molasses per acre.

Condition.		NH$_3$-N.	Nitric-N.	Available-N.	Total-N.	Total-C.	Date of analysis.
Unmolassed	..	0·01206%	0·00344%	0·0155%	0·0603%	0·417%	27-9-35
Molassed	..	0·01228	0·00344	0·01572	0·0608	0·587	,,
Unmolassed	..	0·00768	0·00636	0·01404	0·0609	0·416	12-10-35
Molassed	..	0·01076	0·00436	0·01512	0·0636	0·573	,,
Unmolassed	..	0·00754	0·00636	0·01390	0·0593	0·421	24-10-35
Molassed	..	0·0100	0·00636	0·01636	0·0673	0·507	,,
Unmolassed	..	0·00538	0·00776	0·01314	0·0583	0·418	7-11-35
Molassed	..	0·00896	0·00874	0·0177	0·0667	0·502	,,
Unmolassed	..	0·00502	0·0078	0·01282	0·0583	0·418	13-12-35
Molassed	..	0·0088	0·0088	0·0176	0·0667	0·500	,,
Unmolassed	..	0·00488	0·008	0·01288	0·0574	0·422	10-1-36
Molassed	..	0·008	0·008	0·016	0·067	0·512	,,
Unmolassed	..	0·00464	0·0082	0·01284	0·0572	0·422	11-3-36
Molassed	..	0·00644	0·0082	0·01464	0·0668	0·509	,,
Unmolassed	..	0·0045	0·0082	0·0127	0·0572	0·434	30-4-36
Molassed	..	0·006	0·0084	0·0144	0·0668	0·509	,,

TABLE 45.

69·30 kg. of nitrogen as (NH$_4$)$_2$SO$_4$ per acre of land used and 3000 kilograms of molasses per acre.

Condition.		NH$_3$-N.	Nitric-N.	Available-N.	Total-N.	Total-C.	Date of analysis.
Unmolassed	..	0·02032%	0·00356%	0·02388%	0·0757%	0·416%	27-9-35
Molassed	..	0·02044	0·00384	0·02428	0·0757	0·585	,,
Unmolassed	..	0·00874	0·00932	0·01806	0·0700	0·416	12-10-35
Molassed	..	0·0140	0·00636	0·02036	0·0760	0·574	,,
Unmolassed	..	0·00754	0·01040	0·01794	0·0636	0·416	24-10-35
Molassed	..	0·01272	0·00874	0·02146	0·0823	0·574	,,
Unmolassed	..	0·00636	0·01166	0·01802	0·0612	0·422	7-11-35
Molassed	..	0·0100	0·00972	0·01972	0·0828	0·552	,,
Unmolassed	..	0·00578	0·0116	0·01738	0·061	0·422	13-12-35
Molassed	..	0·0096	0·0098	0·0194	0·0830	0·542	,,
Unmolassed	..	0·0056	0·01144	0·01704	0·0596	0·422	10-1-36
Molassed	..	0·008	0·0100	0·0180	0·0842	0·532	,,
Unmolassed	..	0·0047	0·01176	0·01646	0·0595	0·4234	11-3-36
Molassed	..	0·00656	0·01056	0·01712	0·0844	0·5312	,,
Unmolassed	..	0·0044	0·0117	0·0161	0·0595	0·428	30-4-36
Molassed	..	0·006	0·0106	0·0166	0·0841	0·5321	,,

TABLE 46.

138·60 kg. of nitrogen as $(NH_4)_2SO_4$ per acre of land used and 3000 kilograms of molasses per acre.

Condition.		NH_3-N.	Nitric-N.	Available-N.	Total-N.	Total-C.	Date of analysis.
Unmolassed	..	0·032	0·0028	0·0348	0·14	0·476	18-1-36
Molassed	..	0·032	0·0028	0·0348	0·14	0·7435	,,
Unmolassed	..	0·0080	0·00934	0·01734	0·1081	0·4812	30-1-36
Molassed	..	0·0112	0·00972	0·02092	0·1179	0·7452	,,
Unmolassed	..	0·00582	0·01132	0·01714	0·1032	0·478	19-2-36
Molassed	..	0·0100	0·0100	0·020	0·1185	0·7442	,,
Unmolassed	..	0·00504	0·01194	0·01698	0·0995	0·478	9-3-36
Molassed	..	0·00984	0·0102	0·02004	0·1172	0·744	,,
Unmolassed	..	0·00416	0·01224	0·0164	0·0982	0·478	4-4-36
Molassed	..	0·00956	0·01048	0·0200	0·1092	0·742	,,
Unmolassed	..	0·00324	0·01302	0·01626	0·09212	0·478	25-4-36
Molassed	..	0·00896	0·01104	0·02	0·1012	0·742	,,

TABLE 47.

277·2 kg. of nitrogen as $(NH_4)_2SO_4$ per acre of land used and 3000 kilograms of molasses per acre.

Condition		NH_3-N	Nitric-N	Available-N	Total-N	Total-C	Date
Unmolassed	..	0·0468%	0·0028%	0·0496%	0·200%	0·476%.	18-1-36
Molassed	..	0·0468	0·0028	0·0496	0·200	0·743	,,
Unmolassed	..	0·0234	0·01468	0·03808	0·167	0·481	30-1-36
Molassed	..	0·029	0·01504	0·04404	0·1866	0·745	,,
Unmolassed	..	0·020	0·01488	0·03488	0·1425	0·478	19-2-36
Molassed	..	0·0294	0·01510	0·0445	0·1788	0·744	,,
Unmolassed	..	0·01844	0·01544	0·03388	0·1325	0·478	9-3-36
Molassed	..	0·02774	0·01462	0·04236	0·1725	0·744	,,
Unmolassed	..	0·01784	0·0157	0·03354	0·1281	0·472	4-4-36
Molassed	..	0·0248	0·0164·	0·0412	0·170	0·743	,,
Unmolassed	..	0·00862	0·01848	0·0271	0·1122	0·472	25-4-36
Molassed	..	0·01856	0·02024	0·0388	0·1642	0·742	,,

Thus with 138·6 kg. of nitrogen as ammonium sulphate per acre of land, the loss of nitrogen amounts to 34·2% in the absence of molasses, whilst with molasses it is 27·1%; with 277·2 kg. of nitrogen the loss is 43·9% without molasses, with molasses the loss is only 17·9%.

It will be clear, therefore, that the value of ammonium sulphate as a manure to be used in tropical countries should be greatly enhanced, if it is mixed with molasses, fats or any other carbonaceous material. Recently oil-cakes containing fats and nitrogenous compounds have been found to be effective in tropical countries as nitrogenous manures, because fats are known to retard the oxidation and nitrification of the nitrogenous compounds in the soil. It is clear why farmyard or green manure produces better crop yield than ammonium sulphate alone, because the carbonaceous substances present in the farmyard or green-manure retard the nitrification of the nitrogenous compounds present in the soil and decrease the nitrogen loss. As a matter of

fact, when farmyard manure is added to the soil more nitrogen is conserved and fixed in the soil than with ammonium sulphate. This is evident from the following important results obtained from the Rothamsted fields :—

Total N.

1. Receiving no manure since 1843 .. .. .. 0·095%
2. Receiving farmyard manure since 1852 .. .. 0·256
3. Receiving complete artificials : $(NH_4)_2SO_4$ .. .. 0·099
4. Receiving complete artificials + farmyard manure .. 0·253
5. Receiving potash and phosphate but no nitrogen .. 0·090

Of course, too little oxidation of the protein present in the soil by the addition of molasses will not make the soil suitable for the growth of crops. It seems necessary that an equilibrium should be established between the oxidised and the unoxidised proteins, ammonium salts and other nitrogenous substances which are present in the soil for maintaining its fertility at a proper level. Too much oxidation of the nitrogenous substances and ammonium salts may entail marked nitrogen loss by this type of denitrification and too little oxidation will not make the soil fertile enough for a good yield of crop. Hence the molasses or other carbonaceous substances should not be added in very large amounts, and after the addition of molasses or other substances the soil should be ploughed to help oxidation. Moreover, molasses when added to soil which is properly aerated for helping the oxidation reactions causes nitrogen fixation as is evidenced by the increase of ammoniacal and total nitrogen contents of soil.

This type of nitrogen loss may amount to 100 lbs. of nitrogen per acre annually, whilst the amount of nitrogen required by wheat (for example) per acre is 30–40 lbs. Hence it is highly important to investigate this phenomenon and control this loss without affecting soil fertility.

The greater value of organic nitrogenous compounds for the soil than ammonium salts lies in the fact that not only is the soil texture improved by the colloids added with the organic manure, but the carbonaceous matter added acts as an agent in the preservation of the nitrogenous compounds of the soil by behaving as a negative catalyst.

Apart from this influence of the carbonaceous substances, sugars, cellulose, pentosans, fats, etc. on the conservation of soil nitrogen, these substances when added to the soil along with farmyard or green manure, or straw, also leads to the fixation of atmospheric nitrogen in the soil. Hence the carbonaceous substances, like sugars, cow-dung, cellulose, pentosans, fats, etc. added to the soil are not only effective in nitrogen conservation, but cause nitrogen fixation as well. In a recent article Jenkins has discussed the use of organic manures but has not reported that organic manures help in the conservation and fixation of nitrogen in the soil. This aspect of the importance of organic manures in preference to artificials has been discovered by the present writers.

The foregoing results show that when 17·32 to 69·3 kgs. of nitrogen as ammonium sulphate are added per acre of soil along with molasses, there is

appreciable nitrogen fixation in the soil even in the presence of ammonium sulphate, as the total nitrogen at the end in the fields containing ammonium sulphate and molasses is always greater than at the beginning. These results cannot be explained from the bacterial view point of nitrogen fixation, because it has been assumed that in presence of ammonium salt hardly any bacterial nitrogen fixation is possible. Hence our results showing an increase of nitrogen, when molasses is added to fields to which ammonium sulphate has already been added, support the view that nitrogen fixation is partly bacterial and partly photochemical and catalytic.

Molasses, press mud and oil cakes in the reclamation of alkali land.

The late Dr. J. W. Leather carried on experiments for the reclamation of alkali soils in different parts of the United Provinces. His conclusions are as follows :—

1. ' The only experiment which can claim to have really reclaimed the *Usar* land (alkali land) is the application of gypsum. The cost of sufficient gypsum to effect this was very great—about 700 or 800 rupees per acre—and is obviously prohibitive. Even if the cost of gypsum could be reduced to one-half it would still be too expensive if required in the quantity that this land did receive it.

2. The effect of deep and good cultivation coupled with heavy manuring has not been either what is indicated to the unaided eye or what might have been anticipated. The surface foot of soil has been apparently reclaimed, but below this the soil is as bad as ever.

3. Scraping of the salts is practically useless.'

Compare ' Investigations on *Usar* land in U.P.' by J. W. Leather, Allahabad, 1914, p. 37. Recently Dr. Dalip Singh and Mr. S. D. Nijhawan (1932) have tried to reclaim Kallar (alkaline) soil at Lyallpur, Lalakaku, Montegomary, and Bara Farm by the application of a mixture of gypsum and calcium chloride. The pH of the soil was 9 before the treatment and it became 8·2 after treatment. They reported that the soil permeability appreciably increases on this treatment after 4 years and the process of reclamation takes 4 years, which is also the time required by the application of gypsum or powdered sulphur.

Dr. A. N. Puri is carrying on some experiments in this direction at Lahore. Regarding the success of the work on the reclamation of alkali land in the United Provinces, the following statement of the Director of Agriculture, U.P., is of interest :—

' Usar reclamation experiments were carried on by this Department at Juhi (Cawnpore), and Abbaspur (Unao) without appreciable results and the *Babul* plantations at the places were transferred to the Forest Department. The matter may, therefore, be please referred to that Deptt.'

Vast tracts of land in India are alkaline.

It is estimated that the total area of *Usar* lands in the United Provinces alone is more than four million acres. Dr. J. A. Voelcker, who examined the extent of alkaline lands in Northern India, stated in his ' Improvement of Indian Agriculture ', London, 1893, p. 55, as follows :—

' Enormous areas, especially in the plains of Northern India, are thus affected, and in the North-West Provinces alone there are between four and five thousand square miles of *Usar* land.' In the Punjab (Lyallpur, Montegomary, and other places), Behar, Mysore, Sind, and Bombay, there are vast tracts of such unproductive land. Naturally the reclamation of these lands is a problem of great importance to India. The salts which make these lands unfit for growing crops are the carbonate, sulphate and chloride of sodium, sodium carbonate is chiefly responsible for the unproductiveness of such lands, which are generally heavy clay soils and are very often termed *parti* or waste lands. In Sind and in other parts of the country, normal soils are being converted into alkaline ones by irrigation water. Moreover, there are vast tracts of sea water damaged lands in Bengal, Gujarat, Bombay and Madras Presidencies. Due to various causes the amount of alkaline land is increasing in India.

Defects of alkali lands.

The chief defects of alkali land are :—

1. The alkalinity. We have examined several samples of bad *Usar* lands and we find that the pH is as high as 10·8. Neither *Azotobacter* nor nitrite-formers are observed in cultures obtained with these soils.

2. The amount of calcium compounds is less in these soils than in normal ones. The amounts of exchangeable bases are less than in normal soils.

3. The nitrogen content is small. In several samples examined by us the total nitrogen varied from 0·008 to 0·02%, normal soils contain approximately 0·05% nitrogen.

4. The soil is highly impermeable to water.

5. The soil particles do not settle readily when shaken with water.

6. Lacks bacterial activity.

Molasses, press mud and oil cakes in the reclamation of alkali soils.

Molasses containing acids, carbohydrates, soluble calcium salts, phosphates, potash, etc. can readily remove all these defects of alkaline lands.

Alkaline lands have been successfully reclaimed near Cawnpore, Allahabad and in Mysore by the application of molasses at the rate of 1 to 10 tons per acre and good rice crop has been grown in these reclaimed areas where no vegetation ever grew. We have applied molasses in amounts varying from 2–5 tons per acre of alkali land at Soraon (near Allahabad) and at the Govt. farm, Unao (Oudh) and have obtained excellent results with rice. The

Mysore Govt. has been able to obtain 1,200 to 1,800 lbs. of rice grains per acre of alkaline land using one ton of molasses per acre on plots where crops failed previously. At our suggestion the Agricultural Chemists at Padegaon (Bombay), Cawnpore, Rohtak (Punjab), Sabour (Behar) are reclaiming alkaline land by using different amounts of molasses.

Our results show that for the reclamation of alkali soils of the dry tracts of Northern India and Mysore molasses can be very usefully applied. It is well known that molasses contains between 60 to 70 per cent of carbohydrates, 4 to 5% potash, 2% lime, 0·5% phosphoric acid, 0·5% iron and aluminium oxides and 0·5% combined nitrogen and the rest water. Moreover, molasses is distinctly acidic. Research work carried on in Allahabad, Bangalore, Java, Hawaii and other sugar-producing countries shows that when molasses is added to the soil along with carbonic acid, organic acids, like acetic, propionic. butyric, lactic, etc. are produced in the early stages in the decomposition and partial oxidation of the carbohydrates present in molasses. Consequently the acids present in molasses and those obtained from the decomposition and partial oxidation can neutralise the alkali of the soils rich in alkali. Moreover, the carbonic acid, which is produced in large amounts from the decomposition and oxidation of the carbohydrates, can convert the sodium carbonate into bicarbonate. Also in the process of the escape of carbonic acid from the molassed soil, the latter is rendered porous and its tilth is improved. The investigations at Allahabad show definitely that the moisture content of the molassed soil is appreciably higher than that of the unmolassed one. The lime, which is added to the soil along with the molasses, is rendered soluble by the organic acids formed from molasses and is helpful in the conversion of the sodium soil into a calcium one.

The soluble calcium salts are beneficial in the improvement of the soil tilth by their flocculating power on the clay particles. Moreover, in presence of soluble calcium salts, the permeability of the soil is greatly improved. Our results show that molasses is a better reclaiming agent for alkaline lands than either gypsum or powdered sulphur, as there is nitrogen loss from soils when these latter reclaiming agents are added to alkaline soil, whilst molasses adds nitrogen. The reclaiming effect of molasses is much quicker than that of gypsum or powdered sulphur, because the acids formed from molasses neutralise the alkali quickly and the soluble calcium salts added with molasses improves the tilth and permeability of the soil. It has been reported that four years are necessary for reclaiming alkaline lands on treatment with gypsum or powdered sulphur but with molasses *two to six months* are quite adequate.

Moreover, as the *Usar* lands contain much less total nitrogen, 0·008 to 0·02% as against 0·04% to 0·05%, in normal soils, and as there is nitrogen loss from *Usar* lands on the addition of gypsum or powdered sulphur, it seems improbable that these two substances could be used as reclaiming agents in tropical soils ; they may be suitable for the soils of temperate countries as they contain more nitrogen (0·1% total nitrogen).

We have repeatedly observed that the pink colour of phenolphthalein obtained by adding this indicator to *Usar* soil mixed with water is quickly destroyed by adding molasses.

We have carried on comparative experiments on the permeability of water through alkaline soils when treated with gypsum, powdered sulphur and molasses and we have observed that the permeability is increased to a greater extent on the addition of molasses to alkaline soils than with gypsum or powdered sulphur. Moreover, our experiments show that suspensions of alkaline soils in water readily coagulate with formation of aggregates, which settle very readily on the addition of molasses to the alkaline soil suspensions.

Press mud from sugar factories containing large proportions of carbohydrates and calcium compounds are also very useful in the reclamation of alkali and *Usar* soils. Using ½ to 1 ton of oil cakes per acre, *Usar* soils have been successfully reclaimed for rice cultivation.

Our work on nitrogen transformations in soil has been briefly summarised in ' Nature ' (1936) in the following words :—

' MOLASSES, NITROGEN FIXATION AND LAND RECLAMATION.'

In his presidential address to the United Provinces Academy of Sciences, India, on December 19, 1935, Prof. N. R. Dhar gave a general account of the work carried out by himself and his collaborators on nitrogen transformations in soil. Prof. Dhar leads the school of thought which believes that nitrification in soils and nitrogen fixation from the atmosphere are, especially in the tropics, photochemical, at least as much as bacterial actions. Prof. Dhar has produced strong evidence in support of his theories, and the question appears now to have reached the stage at which the protagonists of bacterial and photochemical nitrification respectively are unwilling to admit any evidence which might shatter their beliefs.

Meanwhile, other soil workers will be wise to keep an open mind on the matter, for the philosophical implications of recognising that light plays a part in soils analogous to photosynthesis in the vegetable kingdom are at least as important as the practical possibilities of utilising that knowledge for the enrichment of the soil. Given sufficient facts, their practical application does not necessarily depend on their correct interpretation. The practical facts of Prof. Dhar's researches are that Indian soils are generally deficient in nitrogen, that more than half a million tons of molasses from the sugar industry are annually wasted in India, and that the application of molasses to the soil can double and may treble the soil nitrogen content, with a consequent large increase in crop yield.

Molasses contains about 70 per cent of carbohydrates and small quantities of nitrogen, phosphorus, potash, etc., these quantities, however, being much too small to account for the observed manurial effect. According to Prof. Dhar, the energy set free in the oxidation of the sugars in molasses is utilised, either bacterially or photochemically, in promoting nitrogen fixation and

nitrification. Whatever the nature of the process, Dhar has produced indisputable evidence of increases in available soil nitrogen and crop yields following the application of molasses. Under temperate conditions, the converse result would be expected, as it is well known that the addition of carbohydrate-rich material to soil tends to reduce the amount of nitrogen available to plants, the nitrogen becoming fixed as microbial protoplasm or as humus. An essential difference, however, between temperate and tropical soil requirements is that, whereas in temperate regions the limiting factor to crop growth is often the slowness, in the tropics it is the rapidity with which soil nitrogen is made available to plants, soluble nitrates being formed and leached from the soil before they can be absorbed by the crop. The general effect of molasses on the soil should be the same everywhere, but only in the tropics will its ' braking ' effect on the mobilisation of soil nitrogen be a positive advantage to the cultivator, and only in the tropics will its stimulation of atmospheric nitrogen fixation, whether bacterial or photochemical, be appreciable, since temperate regions lack the heat necessary for bacterial and the light for photochemical stimulation.

For these reasons, the potentialities of carbohydrate manuring—of which molasses manuring is an example—have perhaps been overlooked by agriculturists. If Prof. Dhar can substantiate his claims, he may effect a revolution in agriculture in India, where the supply of the ordinary organic manures is far below the demand. Prof. Dhar suggests that a most valuable use can be made of molasses in reclaiming alkaline land. The acids produced in the decomposition of molasses neutralise the alkalis, and at the same time and contrary to experience, when land is reclaimed with gypsum or sulphur, soil nitrogen is increased.

A period of about four years is usually necessary to reclaim alkali land with gypsum, whereas with molasses applied at a rate of 30–40 tons per acre, good crops can be grown within six months. It is not stated whether such reclamations have been found permanent—in view of the oxidisability of the neutralising acids, this is open to doubt—but the method obviously merits further study. There are four million acres of infertile alkali land in India, and irrigation practices are increasing the area. The economic reclamation of these lands is one of the country's greatest agricultural problems, to the solution of which Prof. Dhar's work is pointing the way.' *Nature*, April 11, 1936, p. 629.

SUMMARY.

1. Field experiments with molasses, when mixed with soil, show that there is an appreciable increase in the total nitrogen and ammoniacal nitrogen contents. The amount of ammoniacal nitrogen goes on increasing up to a limiting value when it decreases. But at this stage, the nitric nitrogen increases due to the oxidation of the ammonium salts formed from nitrogen fixation and the $C : N$ ratio tends to approach the normal value. This is the time when

crops are to be sown on the molassed fields.   Using 10800 kilograms of molasses per acre of land and digging or turning over once in 15 days, the land is ready for crops in about 12 weeks, with 3600 to 7200 kilograms per acre, it is suitable in about 8 weeks.   If quantities larger than 10800 kilograms of molasses per acre of land are added, about four to five months' interval will be necessary. In all our field trials with molasses as a fertiliser we have always observed an increase of total and available nitrogen.   Moreover, as molasses contains potash, phosphate, lime and as nitrogen is fixed in molassed lands, it is an excellent fertiliser for tropical soils.

2.   When molasses in different amounts is added to soils in dishes and exposed to sunlight and air, the ammoniacal and total nitrogen are also increased.   This increase of nitrogen is always greater in sunlight than in the dark.

3.   When cane sugar solution is added to ordinary soils and exposed to sunlight and air, the ammoniacal and total nitrogen are increased.

4.   When cane sugar solutions mixed with sterilised soil are exposed to sunlight for a long time in quartz vessels under sterile conditions, there is appreciable increase in the available and total nitrogen contents of the sterile soil.

5.   Experiments show that 4 milligrams of nitrogen are fixed as ammonia per gram of glucose or cane sugar oxidised by passing air through solutions of these carbohydrates in presence of ferrous hydroxide.   It appears that the efficiency of nitrogen fixation obtained in the induced oxidation of carbohydrates is of the same order as that with cultures of *Azotobacter* thriving in flasks.

6.   Our experimental results show that in the photochemical or induced oxidation of carbohydrates, nitrogen fixation can take place.   The oxidation of energy-rich organic compounds by air either by light absorption or by chemical induction or catalytic action or by bacterial action causes the fixation of atmospheric nitrogen.   It appears, therefore, that in tropical countries in ordinary soils the fixation of atmospheric nitrogen by the addition of energy-rich compounds is partially bacterial and partially photochemical and catalytic.

7.   Excellent composts containing double the amount of total nitrogen as is originally present in the soil have been obtained by mixing molasses with soil in heaps, which are exposed to air and light.   The soil organic matter and humus and carbon are also considerably increased on the addition of molasses.

8.   The available and total nitrogen of soils, which have been molassed for three consecutive years, are greater than in soils molassed once or twice. It seems, therefore, that molasses exerts a residual effect on the soil.

9.   This new method of nitrogen fixation based on the principle of the utilisation of the energy available from the oxidation of carbohydrates and

other organic compounds in the soil should be largely utilised in tropical countries, where the velocity of the oxidation of substances in the soil is high under ordinary conditions due to the high temperature and light absorption.

10. In cold countries, the soil temperature being low and due to lack of sunshine, the velocity of the oxidation of energy-rich substances present in the molasses may be small and thus the energy available from the oxidation of carbohydrates may be too small for any marked nitrogen fixation. Moreover, in temperate climates, *Azotobacter* is not suitable for nitrogen fixation, as our experiments and those carried on in other countries show that nitrogen fixation by *Azotobacter* at 10° and lower temperatures is practically nothing as *Azotobacter* requires more heat than most other bacteria ; this is why *Azotobacter* has not been utilised by agriculturists in cold countries for nitrogen fixation.

11. *Azotobacter* should be widely utilised in the fixation of atmospheric nitrogen in the soil of tropical countries when fed with energy-rich substances like molasses, press mud, cellulosic substances, etc.

12. Our results obtained with ammonium sulphate added to the soil, with and without molasses, show that the total and available nitrogen of the molassed plots are always greater than those in the unmolassed plots. Hence molasses not only fixes nitrogen in the soil but also acts as a sparer of nitrogen in the soil and this is a very important application of molasses. In tropical countries a mixture of molasses and ammonium salts is a better fertiliser than ammonium salt alone.

13. Cane sugar has also been found to act as a sparer of soil nitrogen. When molasses or cane sugar is added even in large quantities to the soil exposed to light and air, there is no evidence of anaerobic denitrification in all our experiments, although it has been generally believed that in such cases anaerobic denitrification sets in.

14. The moisture content of molassed land is always greater than in unmolassed land.

15. Appreciable amounts of nitrogen fixation have been observed when soil mixed with cellulosic materials like filter paper, dry leaves, cow-dung, etc. are exposed to sunlight for oxidation of the organic substances on the soil surface. Moreover, sodium tartrate, citrate, oleate, palmitate, stearate, etc. when mixed with soil and exposed to sunlight leads to nitrogen fixation.

16. It appears that in aerobic nitrogen fixation through the agencies of bacteria, light, catalysts and chemical induction, the nitrogen and oxygen combine, forming nitrate, which in its turn is converted into ammonia and small amounts of amino acids by the action of carbohydrates.

17. Greater yields of rice and sugarcane have been obtained with molasses as a manure.

18. Our experiments as well as those carried on in Java show that the increased fertility of the soil on the addition of molasses is chiefly due to the

carbohydrates present in the molasses, as an equivalent amount of minerals and combined nitrogen as present in molasses produce very slight effect in improving the crop yield. It is quite clear from our experiments that the nitrogen fixed on the addition of molasses to the soil is the chief cause of the increased soil fertility observed.

19. *Azotobacter* numbers increase in abundance and reach a maximum where they remain more or less stationary and help the fixation of atmospheric nitrogen when molasses or sugars are added to soil. No correlation or direct proportionality between the *Azotobacter* numbers and the nitrogen fixed is observed. In the control plot *Azotobacter* numbers remain more or less stationary.

20. The *Azotobacter* count of the soil exposed to sunlight is always less than that kept in the dark or covered with wooden planks, whereas the nitrogen fixation is greater in the exposed than that in the dark or covered soil.

21. Total carbon of the exposed soil is always less than that of the dark soil, showing thereby that sunlight facilitates the oxidation of energy-rich substances and thus causes greater nitrogen fixation.

22. It has been observed that the maximum fixation (largest amount of ammonia formation) takes place at about 35°, which is, therefore, the optimum temperature for *Azotobacter* isolated from the garden soil at Allahabad, as against 28° obtained in temperate countries. There is hardly any ammonia formation at 10° on the one hand, and at 60° on the other.

The optimum temperature for bacterial nitrification in tropical countries is 35° as against 25° in temperate climates.

23. Experimental results *in vitro* show that ammonium sulphate, mixed with sterilised and unsterilised soils, undergoes nitrification and amino acids added to soil or other catalytic surfaces are oxidised to ammonium salts to a greater extent in sunlight than in the dark.

Similarly, dilute sodium or potassium nitrite solutions are readily oxidised to nitrate when exposed to sunlight. Hence it has been concluded that the whole process of nitrification is accelerated by sunlight.

24. The amounts of available nitrogen varies from 10 to 47·7% of the total nitrogen in soils collected from different parts of India, whilst in English soils it is only one per cent of the total nitrogen.

25. The carbon-nitrogen ratio in soils does not seem to be controlled by the energy requirements of the micro-organisms as advocated by Doryland, but appears to be regulated by the ease with which proteins, amino acids, ammonium salts, etc., are oxidised by air aided by bacteria, inductors, catalysts and light in presence of carbonaceous substances under different conditions, and the oxidations taking place in the soil seem to be guided by the same laws which rule animal metabolism.

26. The carbon-nitrogen ratio in soils rises with increase of the soil temperature.

27.   Marked loss of nitrogen in the gaseous state is observed when nitrogenous compounds are added to soil in which the conditions are favourable for oxidation by aeration. This loss of nitrogen is high when the amounts of nitrogenous manure added is large and can readily exceed the amounts of nitrogen required by crops.

28.   When manures are composted in aerobic conditions there is greater loss of nitrogen than under anaerobic conditions. This type of nitrogen loss is chiefly due to the formation and decomposition of ammonium nitrite and nitrous acid from the nitrification of the nitrogenous substances and in the reduction of nitrate by organic substances.

29.   The decompositions of ammonium nitrite, which can take place in the dark at temperatures from $20°$ upwards, are accelerated by sunlight.

30.   Field trials show that molasses markedly retards the nitrification of ammonium sulphate and decreases this type of nitrogen loss. Moreover, when the amounts of ammonium salts added to the soil are not large, there is appreciable nitrogen fixation in presence of molasses. This nitrogen fixation cannot be explained from the bacterial view point.

31.   Exposure to sunlight causes greater nitrification and nitrogen loss when ammonium sulphate is added to soil in fields.

32.   Organic manures like molasses, leaves and cellulosic materials, green manures, cow-dung, oil cakes, etc., when added to the soil not only increase the moisture retention capacity and improve the soil tilth but also conserve the soil nitrogen and adds nitrogen to the soil by fixation of the nitrogen of the air. Hence fields manured by cow-dung and other organic manures contain more total nitrogen than fields manured by artificials.

33.   Experimental results show that molasses when added to alkali soils and watered converts the alkali soils into acidic ones.

34.   The carbohydrates present in molasses when mixed with soil, which is not sufficiently aerated, are partially oxidised to carbonic acid and partially converted into organic acids (e.g., acetic, lactic, propionic, butyric, etc.). These organic acids neutralise the alkali of the alkali lands.

35.   The soluble calcium salts added with molasses flocculate the clay particles readily, and thus improves the permeability and tilth of the soil. The molassed alkali soil is much richer in microbial activity.

36.   In the oxidation of carbohydrates and the sodium salts of the organic acids obtained from molasses nitrogen fixation takes place and thus the chief defects of alkali soils are remedied quickly by the addition of molasses to alkali soils.

37.   Using one ton of molasses per acre of alkali land the Mysore Government have obtained 1200–1800 lbs. of rice grains per acre of land, where the crop completely failed in previous years.

38.   Comparative results show that a mixture of molasses and press mud is a better reclaiming agent than powdered sulphur and gypsum hitherto used

as reclaiming agents for alkali soil, because on the addition of molasses and press mud the nitrogen deficiency of alkali land is rectified and the nitrogen content of these reclaimed lands comes up to the normal level, whilst on the addition of gypsum or powdered sulphur the alkali soil appreciably loses its nitrogen content.

38. Press mud and different oil cakes have been found to be good reclaiming agents for alkali fields.

PHOTOCATALYTIC REDUCTION OF NITRATE AND THE SIMULTANEOUS OXIDATION OF AMMONIA TO NITRITE.

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It is well known that potassium nitrate decomposes to nitrite in aqueous solution when exposed to ultraviolet light. Warburg [1918] studied the energetics of this reaction. His results showed (1) that the photolysis is more rapid in alkaline than in acid solutions and (2) that the quantum yield is much less than unity and falls off rapidly above 2500 Å. Anderson [1924] stated that this is a process in which a photo-stationary state is reached according to the equation

$$KNO_3 \rightleftharpoons KNO_2 + (O)$$

Anderson's work was criticised by Villars [1927] who denies the existence of a photo-stationary state in this reaction.

When a solution of potassium nitrate is exposed in a glass vessel to sunlight there is no decomposition of the nitrate to nitrite, but if it is exposed to sunlight in a glass vessel together with ignited ferric oxide photolysis takes place. There is no reaction in the dark. It has also been observed that sterilised soil can markedly photocatalyse this reaction. Further, if an ammonium salt was present in the solution, ammonia disappears and there is an increase in the amount of nitrite formed. Thus it appears that the photocatalytic decomposition of nitrite brings about the oxidation of ammonia to nitrite. As these reactions are important for the nitrogen problem of the soil they have been studied in detail in the following investigation.

EXPERIMENTAL.

Ferric oxide was precipitated from ferric sulphate solution, by the addition of the requisite amount of sodium hydroxide solution; the precipitate was washed free from sulphate and alkali; it was dried in a steam oven, powdered and sieved through a sieve of 80 mesh. 100 c.c. of a 0·1 N potassium nitrate solution was exposed with 1 gm. of the ferric oxide in a 500 c.c. pyrex flask. The nitrite nitrogen was estimated from time to time by the Griess-Ilosvay colorimetric method. The following table gives results obtained on the variation of the rate of photolysis with the pH.

TABLE I.

pH	M.gms. of nitrite nitrogen formed		
	20 hrs.	40 hrs.	60 hrs.
7·0	0·21	0·41	
7·58	0·72	1·19	1·5
8·09	0·82	1·36	1·81
8·61	0·97	1·93	2·2
9·08	1·08	2·1	2·56
10·20	1·16	2·30	3·24
10·80	1·86	3·97	4·97

Influence of variations of concentration of nitrate.

The following table shows that the rate of photolysis of nitrate decreases with diminishing concentration of nitrate. The experiments were done at pH 10·8.

TABLE II.

No. of hours of exposure	M.gms. of nitrite nitrogen		
	M/10 KNO$_3$	M/100 KNO$_3$	M/1000 KNO$_3$
20	1·42	. . . .	. . . .
45	2·04	0·54	. . . .
75	3·50	0·66	0·12
100	7·14	1·59	0·19
130	9·03	1·95	0·28

Influence of ammonium chloride.

The following table gives the amount of nitrite nitrogen formed on exposing 100 c.c. of M/10 potassium nitrate with different concentrations of ammonium chloride in the presence of 1·0 gm. of ferric oxide. The experiments were conducted at pH 7·0.

TABLE III.

No. of hours of exposure	Amount of nitrite nitrogen in m.gms. per litre		
	M/50 NH$_4$Cl.	M/100 NH$_4$Cl.	M/200 NH$_4$Cl.
20	0·52	0·45	0·40
45	1·10	0·95	0·85
75	2·20	1·95	1·50
130	8·4	7·77	6·97

Another set of experiments were done at pH 10·8 but otherwise similar to those described before. The results are tabulated thus :—

TABLE IV.

No. of hours of exposure	Amount of nitrite nitrogen in m.gms. per litre		
	M/50 NH₄Cl.	M/100 NH₄Cl.	M/200 NH₄Cl.
20	1·87	1·49	1·29
45	3·73	3·26	2·63
75	6·82	5·97	3·65
100	11·67	10·22	7·41
130	16·53	14·22	11·03

These results show that in the presence of ammonium chloride there is an increased formation of nitrite.

Experiments with soil as photocatalyst.

Waltair red soil was washed with distilled water until free from salts and then sterilised by heating at 160–170°C for 10 hours.   It was then powdered and passed through a 40 mesh sieve.   This was used as a photocatalyst.

100 c.c. of potassium nitrate solution were exposed to sunlight in a pyrex flask with 5 gms. of red soil.   The results at different pH values are recorded below.

TABLE V.

pH	M.gms. of nitrite nitrogen per litre		
	20 hrs.	40 hrs.	60 hrs.
9·6	3·33	4·7	6·31
10·2	3·46	4·93	6·60
10·8	3·54	5·15	7·00

Influence of ammonium chloride on the photo-decomposition of nitrate.

The following table shows the amount of nitrite nitrogen formed when 100 c.c. of M/10 potassium nitrate solution was exposed with different concentrations of ammonium chloride in the presence of 5 gms. of soil at pH 7·0.

TABLE VI.

No. of hours of exposure	M.gms. of nitrite nitrogen formed		
	M/50 NH$_4$Cl.	M/100 NH$_4$Cl.	M/200 NH$_4$Cl.
20	1·75	1·42	1·26
45	2·63	1·81	1·67
75	3·59	2·69	2·38
100	7·87	5·97	4·83
130	13·93	10·40	9·01

In one set of experiments the estimation of ammonia nitrogen was made and it was found that this figure decreased progressively. However, there was more loss of ammonia than could be accounted for by the increase in the nitrite content over the blank. Further work is in progress on different aspects of the problem.

The photo-oxidation of nitrite to nitrate.

Dhar and co-workers [1934, 1936] have observed that sodium nitrite in aqueous solution is oxidised to sodium nitrate when exposed to sunlight in the presence of zinc oxide, titania, or ferric oxide. Sarkaria and Fazal-uddin [1933] have also found that sodium nitrite is oxidised to nitrate photocatalytically in the presence of animal charcoal or ferric oxide. We have now found that sterilised soil can also act as a photocatalyst. In the following experiments 100 c.c. of 0·001 molar sodium nitrite solution was exposed to sunlight with 5 gms. of sterilised soil at different pH values.

TABLE VII.

No. of hours of exposure	M.gms. of nitrite nitrogen remaining per litre		
	Exposed at pH 7	Exposed pH 8·61	Exposed at pH 10·8
. .	14·0	13·90	14·00
40	12·10	12·60	12·75
75	9·83	10·76	12·13

It appears from these results that the rate of oxidation decreases as the pH is increased. On the other hand the photo-reduction of nitrate to nitrite is faster in alkaline than in neutral or acid media. It must be noted in this connection that the oxidation of nitrite to nitrate occurs in the dark when the medium is definitely acidic ; no oxidation, however, takes place at

pH 7 and above. In sunlight, however, there is appreciable oxidation even in alkaline media when catalysed by ferric oxide or sterilised soil.

In previous publications Gopalarao and Dhar [1931] and Gopalarao [1934] have suggested that nitrification in soils is partly a photo-chemical reaction taking place at the surface of the soil under the influence of sunlight. Corbet [1934, 1935] is also of the opinion that nitrification in soils, specially those of the tropics, is a photo-chemical reaction.

As shown above potassium nitrate in aqueous solution can decompose to nitrite in light transmitted by glass provided ferric oxide is used as a photo-catalyst. The decomposition of nitrate is an endothermal reaction occurring with the absorption of energy (81 kilocalories)

$$NO'_3 \rightarrow NO'_2 + (O) - 81 \text{ kilocalories.}$$
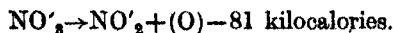
This corresponds to radiation of wavelength 3500 Å. The experiments of Warburg [1918] have shown that the quantum yield with radiation of 2070 Å is only 0·25 while with 2820 Å it is much lower, e.g. 0·024. Thus it appears that as the wavelength of the light is increased the quantum yield rapidly decreases. Our observations show that in the presence of a suitable heterogeneous catalytic surface, e.g., ferric oxide or sterilised soil, the energy of activation is considerably lowered thus making it possible for the reaction to occur in visible light. The mechanism of this photocatalytic action raises questions of theoretical interest which are beyond the scope of this paper and will be discussed elsewhere.

The observations that sterilised soil also acts as a photocatalyst, and that if an ammonium salt is present the ammonia is simultaneously oxidised to nitrate, lend further support to the photochemical view of nitrification put forward in earlier publications.

We have also noticed that nitrate can be oxidised to nitrite photochemically in the presence of ferric oxide. It thus appears likely that many reactions hitherto supposed to be due entirely to the action of bacteria can also be brought about by sunlight with soil as photocatalyst.

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FLUCTUATIONS, RECUPERATION AND FIXATION OF NITROGEN IN THE SOILS OF WESTERN INDIA.

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I

This paper gives a short account of the work done on soil nitrogen at the laboratory of the Agricultural Chemist to the Government of Bombay, Poona.

The problem as to how the fertility of Indian soils is maintained in the absence of manure, more particularly in the arid and semi-arid tracts like the Deccan, has always been a difficult one. More especially the maintenance of the available nitrogen is difficult to explain. On the one hand, there is a demand on the accumulated stocks of nitrogen from the crop grown. This reaches, in the case of an annual crop of Jowar (*Andropogon Sorghum*) grown without manure, to about 20 lbs. of nitrogen per annum for such a crop (700 lbs. grain and 2,000 lbs. straw) as is commonly produced in the Bombay Deccan. Then there is the annual loss from drainage and from denitrification.

It would seem certain, therefore, that even in the absence of vegetation, there must be considerable fixation of nitrogen from the atmosphere.

The soil used for the work was obtained from Pashan village, five miles from Poona. It had been cropped every year, but without any leguminous crop or any manure for ten years. There had likewise been no irrigation, and the annual crop was either Bajri (*Pennisetum typhoideum*) or Jowar (*Andropogon Sorghum*). It was a typical 'medium black soil' of the Deccan.

To begin with, it was decided to find out the effect on the nitrogen of the soil of varying the quantities of moisture, and also of varying the temperature and the light conditions of the soils, and also the effect of additional lime in each of these cases.

Effect of varying the quantities of moisture.—The following table gives the milligrammes of organic and ammoniacal nitrogen per 100 grm. of soil kept at 20°C. in the incubator.

TABLE I.

	1st day	After 35 days	After 70 days	After 105 days	After 140 days	After 175 days
	Milligrammes per 100 grm. of soil					
Soil containing 30 per cent moisture.	33·01	48·55	35·18	30·73	25·00	26·21
Soil containing 20 per cent moisture.	33·01	42·00	33·79	30·77	..	23·93
Soil containing 6·6 per cent moisture.	33·01	31·38	29·80	25·61	22·64	..

From the above table it is evident that the higher the quantity of water the higher is the amount of nitrogen fixed. It seems that during the first thirty-five days nitrogen is fixed and then during the next period the amount decreases. After this also it continues to go down upto at least 175 days. It must be remembered that the figures present the algebraic sum of the fixation and the loss of nitrogen, since both these actions are likely to go on side by side. It is also possible that the smaller figures may be due to nitrification.

Effect of temperature.—The trays kept at 20°C. represent a low temperature, those at 40°C. represent a high temperature, while those kept in diffused light were between 20°C. and 27°C. for the first three months and therefore represent an intermediate stage. After 35 days all the samples show a fall in the nitrogen contents, and hence the figures for the first 35 days only are shown in the following table. The figures are in milligrammes of organic and ammoniacal nitrogen in 100 grm. of soil.

TABLE II.

	30 Per cent moisture	20 Per cent moisture	6·6 Per cent moisture
	Milligrammes per 100 grm. of soil		
40°C.	55·01	44·31	35·21
Diffused light	49·98	47·07	38·14
20°C.	48·55	42·00	31·38

These figures clearly indicate that the largest quantity is fixed at a temperature above 20°C., but at 40°C. it is lower than at temperatures between 20°C. and 27°C. It seems that a high temperature like 40°C. slackens the activity of fixing nitrogen or hastens nitrification.

Effect of additional lime.—First set. To find out the effect of additional lime, three per cent of calcium carbonate was added to the soil although it already contained excess of calcium carbonate.

The experiment showed that additional lime brings about more nitrification, but the total nitrogen throughout the period of 84 days is greater in the original than in the same soil with additional lime.

Effect of light.—From the results obtained during the experiments no definite relation of the increase of nitrogen to the intensity of light can be shown, but it is certain that even in darkness the fixation goes on.

In the first two series it was found that after about thirty-five days from the time of exposing the samples, the highest figure for increase of nitrogen was obtained and after that there was a regular fall. When the soil was taken for experimental purposes it was air-dry containing about 6 per cent water, and it was this soil that showed fixation when water was added. It seems,

therefore, that when a dry soil gets water it begins to show this activity of fixing nitrogen. In order to find out the extent to which this property proves to be useful in increasing the nitrogen contents of the soil a third series of experiments was taken up.

The conclusions that can be drawn from this series are :—

When the soil gets water the nitrogen begins to increase for some time and then a fall commences. If at this juncture the soil is dried at 60°C. and then gets moistened again, the nitrogen increases further, for four and five weeks more, and then begins to go down. Repeated drying does not increase the nitrogen contents beyond a certain limit under the given conditions.

II

This is only a continuation of part I. It gives the results of experiments done with different typical soils of the Bombay Presidency. It also records the results of experiments done to find out the effect on nitrogen recuperation of added (a) lime as calcium carbonate, (b) phosphatic substances, (c) organic matter and (d) alkali salts.

The soils alone or with additional substances were kept at 35°C. in an incubator. All the soils had water equal to one-third the water-holding capacity.

Effect of addition of lime.—In order to ascertain the effect of additional lime on soils with different percentages of original lime, experiments were done on Goradu soil from Nadiad, River silt from Poona, and Laterite soil from Belgaum by adding 3 and 5 per cent of calcium carbonate.

TABLE III.

	Original lime as CaCO₃	pH value	Nitrogen fixed per 100 grams. of soil over the original nitrogen
	Per cent	Per cent	Per cent
Medium black soil	7·96	8·35	21·17
Goradu soil	2·36	8·22	6·36
River silt soil	1·30	8·18	5·6
Laterite soil	0·44	5·99	2·17

TABLE IV.

Soil	Original lime per cent as calcium carbonate	Milligrams of nitrogen fixed over that in the control	
		3 per cent lime added	5 per cent lime added
	Per cent	Per cent	Per cent
Medium black soil	7·96	*nil*	*nil*
Goradu soil	2·36	2·6	2·71
River silt soil	1·30	4·09	8·70
Laterite soil	0·44	4·55	8·40

As shown in series I, the Medium black soil which already contains a high proportion of lime is not benefitted at all by additional lime while all the other soils are benefitted.   In Goradu soil with 2·36 per cent of original lime, addition of 3 per cent shows some increase in the power of recuperation, but 5 per cent addition does not show any distinct advantage over 3 per cent, because the addition of 3 per cent is enough to make up the required proportion of lime and the extra 2 per cent has, therefore, no effect.

Effect of Phosphatic Substances.—Phosphoric acid is one of the important plant food constituents.   In a suitable form it is found to be beneficial to the crops and to small organisms.   The addition of phosphorus to a soil has been found to increase the amount of nitrogen fixed.

If phosphoric acid, in the form of superphosphate, is added to soils their nitrogen recuperation power is increased.   In the quantities used, the larger quantity of phosphoric acid has a better effect than the smaller quantity.

Effect of addition of organic matter.—Goradu, River silt and Laterite were the three soils selected for experiment.   They contain different proportions of organic matter.   Cane sugar was added in solution in two proportions —2 per cent and 4 per cent.   Water was added to make up to one-third the water-holding capacity of each soil and all the samples were incubated at 35°C.

Addition of 2 per cent sugar shows a beneficial effect in increasing nitrogen fixation power and a further addition of 2 per cent shows a further small advantage with the three soils under experiment.   The smaller the proportion of original organic matter the greater is the effect of added organic matter. Addition of sugar has a deleterious effect on the nitrifying power of the soil at least for some time.

The alkali salts—sodium carbonate, sodium sulphate and sodium chloride —when added to medium black soil of the Deccan, and Goradu and Laterite soils show a deleterious effect on the nitrogen recuperation power of these soils.   Sodium carbonate is the most and sodium chloride the least harmful of the three.

The alkali salts have the worst effect on the medium black soil while their effect is the least on the Laterite which is an acidic soil.   The alkali salts with the quantities used in the experiments show a stimulating effect on the nitrogen recuperation power of the River silt soil.

The River silt which is a freshly deposited soil is easily stimulated by the addition of lime, phosphoric acid or organic matter and is also stimulated by the addition of small quantities of alkali salts in increasing its nitrogen recuperation power.

III

The above results definitely prove that, at least under the controlled conditions of the laboratory, the additions of phosphatic substances and organic

matter improve the nitrogen recuperation of such soils as are not originally rich in these ingredients. But it remained to be seen whether any recuperation of nitrogen takes place actually under field conditions where there is repeated wetting and drying of soils by rain and heat. It was therefore necessary to determine whether the fixation of nitrogen takes place under field conditions, just as it does in the laboratory. Such a suitable place was found at the Dry Farm Experiment Station at Manjri about 8 miles to the east of Poona. Under the dry arid conditions of the Deccan nitrogen is liable to far greater losses than any other plant food ingredients and from 1927 onwárds nitrogen deter-minations were made every year sometime after the harvest of the crop.

The figures indicated rapid depletion of soil fertility. But the decrease in nitrogen contents of the soil was not found to have resulted in lowering. the yields from these plots. Further, there was a similar depletion of nitrogen from a plot which received farm yard manure.

It was therefore decided to carry on a series of determinations of the total nitrogen contents of soils receiving different treatments of cultivation and manuring throughout one complete year taking the soil samples once every month.

It is interesting to trace the change in nitrogen content of well cultivated plots in comparison with the actual soil temperatures observed together with the moisture contents of the soil from month to month as given in the table below :—

Total nitrogen in 9″ surface soil together with corresponding soil moisture and average monthly soil temperature.

TABLE V.

Months	Total nitrogen milligrams in 100 grammes of oven dry soil	Per cent moisture	Average monthly soil temperature ; average of tempera-ture at 3 and 6 inches depth from surface
July, 1930	73·6	25·6	27·3
August, 1930	98·1	24·1	28·6
September, 1930	80·9	28·1	27·4
October, 1930	99·4	25·9	29·5
November, 1930	102·1	22·3	27·8
December, 1930	121·6	20·2	29·5
January, 1931	118·3	17·7	30·4
February, 1931	118·3	14·4	31·9
March, 1931	108·7	11·3	34·4
April, 1931	107·9	8·0	39·3
May, 1931	100·6	13·6	40·3
June, 1931	105·8	16·3	....

When the determinations were commenced just after the middle of July the monsoons had just set in and had moistened the upper six-inch layer of the surface soil. The soil temperatures which were high, going up to 40°C., had come down giving an average soil temperature of 27·5°C. The nitrogen content of the soil was then at its minimum being 73 milligrams per hundred grammes of the soil. The effect of wetting by the monsoon rains together with a slight rise in soil temperature was to increase the nitrogen to 98 milligrams or a rise of 33 per cent in a month's period after the original determination. The heavier rain in the month of September amounting to 5·75 inches, combined with a fall in temperature by over a degree, resulted in lowering the nitrogen content to 80 milligrams or fall of 17 per cent over the previous determination. The next determination again showed an increase in nitrogen to the extent of 34 per cent over the original. There was a little more than 3″ of rain during this period but the average temperature had increased by over 2°C. In the following month there was a slight rise in nitrogen but the peak of the curve reached its highest in December. There was practically no rain between the determinations of November and December and the average soil temperature was higher than ever before, since the commencement of the experiment. The maximum rise in nitrogen contents was as much as 65 per cent over the original. During the next two months the nitrogen remained fairly high under the high temperature of January and February. Then a steady fall in nitrogen continued throughout the following four months from March to June with a steady lowering of the moisture contents of the soil, though there was a steady rise in temperature. At the end of the twelve months period of experiment the soil was left richer in its nitrogen contents than at the commencement, being nearly 43 per cent higher. The land was occupied by a crop of *Rabi Jowar* from the 17th of September 1930 to the 14th of February 1931. In spite of the presence of the crop on the land, it was freely exposed to the sun, rain and wind, as the plant population on the experimental plot was very limited. The crop was sown by dibbling 2 seeds 18 inches each way. The roots and leaves of the plants if obtained in the soil sample were carefully picked up and removed so as to avoid any addition of nitrogen due to their inclusion.

Nitrate and nitrite nitrogen.—It is interesting to see the nitrate and nitrite nitrogen changes in the soil under field conditions. Nitrogen in these forms was probably at its lowest on the starting date. But in a month's period it reaches its maximum peak in August. The moisture content of the soil during this month was about 24 per cent and the temperature was rising. The moist soil was stirred on the 28th July after the first determination. Under those conditions nitrification took place very vigorously and gave the maximum figure for nitrate nitrogen. The moist soil had undergone stirring twice during October on the 1st and 16th of that month and once again in November on the 11th and as a result the nitrate nitrogen again increased during October and November when a second peak was obtained. It decreased considerably

in the following month and remained practically low throughout the cold weather months of January, February and March. Ploughing the land in March and subsequent slight wetting of the surface soil raised the nitrate nitrogen in the following three months of April, May and June. Clarke and his associates also found two peaks for nitrate accumulation under the climatic conditions of the United Provinces.

The first series of determinations described was done on a piece of land which was under a crop receiving special care, attention and treatment. But an ordinary cultivator is not likely to follow the procedure and treatment of land as given there and hence a second series of determinations was made from a piece of land that had a crop grown according to the methods followed by an average Deccan cultivator. The main difference lies in the fact that the cultivator's plot was stirred on a less number of occasions, and had a higher density of plant population, than the specially treated plot and also had some weeds.

The maximum rise in nitrogen contents was nearly the same as on the controlled experimental plots. It was reached in December as in the case of the first series. The chief difference noticed was the sudden fall in nitrogen in one month's period after reaching the maximum and the amount of nitrogen after this fall was comparatively lower than in the former series. At the end of the year's period the nitrogen left in the soil was about 23 per cent lower than that with which the series was started.

The results of the investigation of the second group of plots dealing with three series receiving organic matter added in the form of farm yard manure and green manure or *Crotalaria juncea* may be summarised as follows :—

(1) Nitrogen contents of the soils treated with organic matter showed changes very similar to those observed in untreated soils. (2) The total increase or gain in nitrogen content over the original was, however, much greater in these series than in the series receiving no organic matter. (3) The time of maximum increase was a month or two earlier in the case of addition of farm yard manure or of *sann* in the year of experiment. (4) Where the addition of *sann* was done two years before the experiment the activity and changes in nitrogen contents were very similar to those of unmanured series. (5) There was no substantial difference in the form of nitrates and nitrites except the fact that the maximum peak of nitrate contents was reached later in October or November in cases where additions of organic matter were done freshly. In the case of residual organic matter, the nitrate and nitrite nitrogens behaved exactly as those in the unmanured series.

Definite recuperation of nitrogen takes place in the soils under field conditions in the dry farm tracts of the Bombay Deccan. Wetting of the soil by the monsoon rains and the subsequent partial drying and heating during the dry spells of the monsoon seems to be favourable for starting the recuperation process. Better cultivation of the land helps to maintain the

nitrogen contents of the soil fairly high and does not allow a sudden drop after the maximum peak is reached.

The nitrogen content of the soil is not a stable or a constant quantity. There is a range in every soil depending upon such factors as the moisture, temperature and aeration, which in their turn are dependent upon the climatic factors. Hence the determination of nitrogen contents of a soil without any attention to the time or season of sampling or other concomitants like the moisture and temperature is not likely to throw much light on the fertility of the soil as far as this ingredient is concerned.

IV

The soils on which the above work was done were brought under cultivation only in 1924, before which they were occupied by jungle shrubs. The crop grown on those soils was *Rabi Jowar* (cold season). Further investigation was carried on to find out what fluctuations in soil nitrogen take place under other conditions of climate and soil treatment. Three places were chosen for experiments.

At Poona (rainfall 33·55 inches, 902 mm., 1933) the soil is all from the Deccan trap. One set of experiments was on a soil with a four-month rainy season crop and the other on a soil with an eight-month crop of turmeric under irrigation.

At Belgaum (rainfall 61·6 inches, 1563 mm., 1933) the soil on which the experiments were made was a mixture of material derived from both trap and laterite. On this soil the practice is to grow three crops. The first is a rainy season crop of rice and then there are two others of vegetables grown one after another under irrigation.

At Karjat the soil is derived from trap. The tract receives the heavy rainfall of 154·12 inches (3910 mm., 1933) from June to October. A rainy season crop of rice is grown.

For comparative results both uncropped and cropped plots were studied in each case. Twelve soil samples were taken from each plot every month for 13 months and nitrogen in various forms was determined. Sampling and working errors were ascertained.

Annual cycle of nitrogen fluctuations.—The results obtained show that there are nitrogen fluctuations from month to month and there is an annual cycle of fluctuations for all soils.

Nitrogen and organic matter.—By comparing the total nitrogen figures for uncropped and unmanured plots it is seen that both the highest and the lowest levels of total nitrogen are higher in soils with a large proportion of organic matter than in those with a smaller proportion of organic matter.

TABLE VI.

Relation of organic matter to total nitrogen in soils.

Plots			Organic matter per cent	Per 100 grams of oven dry soil	
				Highest total nitrogen. Milligrams	Lowest total nitrogen. Milligrams
Poona	..	..	..	1·53	51·07	41·22
Karjat	..	..	..	1·81	86·29	81·19
Belgaum	..	..	..	4·44	236·47	197·69

Seasons of highest and lowest levels of nitrogen.—The highest point of total nitrogen reached by a soil may depend on many factors, but in the climatic conditions of the Bombay Deccan the values are high during the cold season between November and February. Although the minimum temperatures in these months are low, they are not so low as to interfere with the reactions of the soil. The maximum temperatures and the moistures in this season, taken together, are favourable for soil reactions. Sometimes another high figure for total nitrogen is obtained in June when the soils heated during summer are wetted by June rains. The total nitrogen is generally low in May when the moisture goes very low. Sometimes very low figures of total nitrogen are found in the middle of the rainy season—July to August—due perhaps to heavy washing.

Seasons of highest and lowest nitric nitrogen.—It was observed that both in the cropped and the uncropped plots nitric nitrogen is high in the cold season when the temperature and moisture taken together form a favourable condition for nitrification. The lowest figures for nitric nitrogen are found in the middle of the rainy season when the nitrates are likely to be washed away. The nitric nitrogen is higher in the uncropped than in the cropped plots.

It was observed in the previous experiments done in connection with the nitrogen recuperation of soils that the cropped rice plot showed more nitrogen than the uncropped rice plot during the growing period of the rice crop. These results have been confirmed by the field experiments in the winter season at Karjat and Ratnagiri and in the rainy season at Karjat.

These results received further confirmation by the experiments done in the laboratory which show that the rice soils have the power of fixing nitrogen and this fixation is helped by the presence of the growing roots of the rice plant. It has been shown that the rice seed does not carry within it any nitrogen fixing organisms.

THE VICISSITUDES OF NITROGEN IN THE SOIL SYSTEM.

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Several workers on soils in different parts of the world have observed loss of nitrogen from the soil in ways other than through drainage. There is a general concensus of opinion that nitrogen undergoes loss in gaseous form to a greater or less extent under field conditions.

Loss of nitrogen is usually explained in terms of carbon-nitrogen ratios, which concept originated from studies on ammonification and nitrification under a variety of conditions. The causes leading to the loss of total nitrogen in the soil do not, however, appear to have been clearly understood. Large quantities of nitrogenous fertilisers are bought and applied to the soil. If nitrogen is to be bought and put into the soil only to be lost into the air, it is bad business. It is one thing if the readily soluble and available nitrogen added to the soil is converted from current account into capital or fixed deposit account, as it were, and it is another thing to lose it as a result of exchange fluctuations.

In the course of investigations by the writer on the nitrification of cattle manure, green manure and ammonium sulphate under field conditions in Coimbatore soils, data were obtained which are difficult of explanation in terms of the usually accepted views. The rate of nitrification and accumulation of nitrates was, as would be expected, greatest with ammonium sulphate, least with cattle manure and intermediate with green manure. Taking 100 for the nitrification value of ammonium sulphate under field conditions, the relative rates for green manure were 50 and 25 respectively in the first foot layer of the soil. From fortnightly examinations extending over a period of three years, it was evident that there was a periodical loss of total nitrogen in the soil under all the manurial treatments but that it was greatest with ammonium sulphate. Similar fluctuations were noticed in unmanured plots also but to a lesser degree. It was ascertained that there was no movement of nitrogen into the deeper layers and there was no moisture saturation leading to denitrification. The following statement shows periodical increase or decrease of nitrogen over the corresponding unmanured plot.

TABLE I.

Periodical increase or decrease of nitrogen over the corresponding
unmanured plot.

(In parts per million of dry soil.)

Date of sampling	Green manure		Cattle manure		Ammonium sulphate	
	Nitric nitrogen	Total nitrogen	Nitric nitrogen	Total nitrogen	Nitric nitrogen	Total nitrogen
Season 1930-31.						
31st October, 1930 ..	+3·6	+27·7	+3·7	+26·4	+4·7	--48·1
13th November, 1930 ..	--0·6	+20·7	--2·4	--16·1	--0·3	--0·7
8th December, 1930 ..	+1·8	+19·4	--0·1	+37·5	--0·2	+14·2
27th January, 1931 ..	+3·7	+44·1	+1·9	+29·5	+3·0	+0·0
13th February, 1931 ..	+6·5	+52·7	+4·8	+65·2	--0·6	+4·2
2nd March, 1931 ..	+3·5	--50·5	+1·0	--58·4	+0·2	--71·5
13th March, 1931 ..	+7·8	+6·5	+3·4	+34·5	+1·8	--7·2
20th April, 1931 ..	+6·1	--51·0	--6·1	--22·0	--3·5	--34·0
	+32·4	+69·6	+6·2	+96·6	+5·1	--143·1
Season 1929-30.						
3rd October, 1929 ..	--4·1	--15·0	--1·6	--28·0	+20·1	--47·0
21st October, 1929 ..	+7·8	+6·0	+12·3	--2·0	+8·1	--28·0
9th November, 1929 ..	+5·6	+101·1	+0·4	+47·0	+2·4	+23·0
25th November, 1929 ..	+6·4	--10·0	+6·6	--26·0	+12·6	--38·0
6th December, 1929 ..	+8·2	--1·0	+2·9	+7·0	+32·5	+15·0
24th January, 1930 ..	+6·6	+12·0	+0·1	--1·0	+6·1	--20·0
8th February, 1930 ..	+9·2	+35·0	--4·4	--16·0	--4·9	--30·0
24th February, 1930 ..	+7·2	+1·0	+1·6	+33·0	+21·1	+29·0
21st March, 1930 ..	--4·3	--10·0	+1·0	--13·0	--4·9	+8·0
	+42·6	+119·1	+18·9	+1·0	+93·1	--88·0

The usual explanation for nitrogen fluctuations is that, when easily decomposable organic matter is added to the soil, biological processes begin to operate immediately the requisite nitrogen for the development of the organisms is obtained from the soil if present in sufficient amount, or from the atmosphere in case of insufficient supplies in the soil. On this basis, the loss in total nitrogen is rather difficult to explain. The nitrogen loss followed the peak values for nitrate accumulation. The influence of carbon-nitrogen ratio might have been felt in the early stages of the decomposition of the materials added, but it is not clear how the loss of. nitrogen, which appears to have occurred chiefly in the end product stage, can be connected with the carbon-nitrogen ratio.

In order that this relationship, if there is any, may be intelligible, the mutual effects of soluble and readily available carbonaceous and nitrogenous substances have been investigated. Cane sugar and sodium nitrate have been used in different proportions to give varying carbon-nitrogen ratios ranging

from 20C : 0N to 0C : 1N. The ratios were obtained by keeping the amount of nitrogen constant and adding the requisite amount of cane sugar to make up the different ratios. The results are given in the statement below.

TABLE II.

Changes in nitric nitrogen under different carbon nitrogen ratios.

Percentage of nitric nitrogen on soil dried at 105°C. to 110°C.

A period	Control	20 : 0	20 : 1	15 : 1	10 : 1	5 : 1	1 : 1	0 : 1
At start	*nil*	*nil*	0·101	0·102	0·103	0·104	0·105	0·106
After 10 days	,,	,,	0·022	0·049	0·048	0·059	0·099	0·106
,, 20 ,,	,,	,,	0·029	0·042	0·050	0·060	0·098	0·103
,, 30 ,,	,,	,,	0·025	0·042	0·061	0·070	0·099	0·107
,, 40 ,,	,,	,,	0·035	0·050	0·065	0·066	0·097	0·104
,, 50 ,,	,,	,,	0·043	0·045	0·064	0·085	0·097	0·106

Total nitrogen content at different periods.

	Control	20 : 0	20 : 1	15 : 1	10 : 1	5 : 1	1 : 1	0 : 1
At start	0·075	0·073	0·171	0·181	0·176	0·177	0·176	0·180
After 10 days	0·078	0·104	0·161	0·148	0·159	0·164	0·159	0·160
,, 20 ,,	0·077	0·108	0·153	0·168	0·166	0·170	0·177	0·159
,, 30 ,,	0·085	0·111	0·154	0·164	0·165	0·161	0·170	0·168
,, 40 ,,	0·079	0·111	0·156	0·143	0·164	0·165	0·171	0·171
,, 50 ,,	0·080	0·111	..	..	..	..	..	..
Percentage change control versus the rest ..	+6·7	+49·3	—6·9	—13·1	—7·4	—6·8	—4·1	—8·3

As the substances added were cane sugar and sodium nitrate, both of which are readily attacked by micro-organisms in the soil, the maximum change in total nitrogen occurred in ten days from the start of the experiment.

A gain in total nitrogen occurred in the absence of added nitrogen to the extent of about 50 per cent, evidently due to fixation of atmospheric nitrogen. In all other cases, there were varying degrees of losses. With nitrate only and no organic matter, there was little change. In the presence of both nitrate and sugar definite loss in total nitrogen occurred, the amount of loss generally increasing as the ratio was narrowed.

In regard to nitric nitrogen, its fluctuation appears to have been regulated by the carbon-nitrogen ratio. The wider the ratio, the greater was the loss. It should be noted that loss in nitrate need not mean loss in total nitrogen. With the 20C : 1N ratio, the loss was about 78% and as only 10 per cent of the total nitrogen is lost, the balance should be assumed to have been absorbed by the micro-organisms. At the other extreme in 0C : 1N ratio the added nitrate nitrogen stood stationary throughout. This evidently could not be utilised by the micro-organisms. It is, therefore, difficult to explain the loss of 8·3 per cent in this case.

Organic carbon was estimated periodically as was done in the case of nitrogen. The position at the end of 50 days showed varying degrees of loss as is seen in the statement below.

TABLE III.

Treatment				Maximum loss of carbon	
				% on total	% on added
Control	..	..	..	..	5·4	....
20C : 0N	..	..	..	..	51·9	74·5
20C : 1N	..	..	..	..	50·6	74·2
15C : 1N	..	..	..	..	47·9	77·9
10C : 1N	..	..	..	..	39·8	77·6
0C : 1N	..	..	..	..	8·4	....

Loss of carbon had taken place in all the series and the greatest loss occurred during the first ten days. The loss during the subsequent period was correspondingly small.

When the loss of carbon is calculated as a percentage of the total carbon content in the soil the loss appears to be a function of the C : N ratio. But when it is worked out as a percentage of the amount of the organic matter actually added a totally different state of affairs is revealed. It will be seen that, regardless of the C : N ratio or of the amount of carbon added, the amount of carbon lost is fairly constant, about 70 to 80 per cent of the added carbon. It should, however, be noted that the carbon-nitrogen ratio ultimately assumes a ratio round about 10 irrespective of the initial magnitude.

TABLE IV.

			C : N on total C and N.		C : N on organic C & N	
			Initial	Final	Initial	Final
Control	..	..	12·8 : 1	11·1 : 1	10·9 : 1	9·9 : 1
20C : 0N	..	..	39·0 : 1	12·5 : 1	37·5 : 1	11·5 : 1
20C : 1N	..	..	16·8 : 1	9·5 : 1	39·4 : 1	11·1 : 1
15C : 1N	..	..	13·2 : 1	8·9 : 1	29·1 : 1	12·2 : 1
10C : 1N	..	..	10·6 : 1	6·8 : 1	24·1 : 1	9·9 : 1
0C : 1N	..	..	5·3 : 1	5·1 : 1	11·4 : 1	11·3 : 1

For a clearer understanding of the processes involved, the soil cultures may be conveniently classified into the following three groups, viz.,

(1) soil cultures containing sugar only and no nitrate ;
(2) cultures containing sugar and nitrate in different proportions ;
(3) cultures containing only nitrate.

Considering the first group, it will be seen that loss of carbon has been associated with a gain in nitrogen, the latter being obviously obtained from the atmosphere to maintain the ratio at about 10 : 1. Now the question arises whether this fixation of atmospheric nitrogen could again be started by the addition of more organic carbon and how far this process could go.

As regards the second group, the introduction of nitrate into the soil along with sugar has resulted in a loss of nitrogen. The biological agencies seem to be entirely different. Nitrogen fixing organisms of the *Azotobacter* type have either changed their functional characteristics or entirely new kinds of organisms have come to the front under the new environment.

The loss of nitrogen is rather difficult to explain since the two essential conditions for denitrification, viz. absence of oxygen and presence of easily oxidisable organic matter are not satisfied in the laboratory experiments. Photo-chemical decomposition can explain fixed losses but there must be some other factor operating in the case of the laboratory experiments.

It would be interesting to find what would happen if the C : N ratio is altered by keeping the carbon constant and changing the nitrate content. It might be expected that since the amount of carbon decomposed is constant, the amount of nitrate converted into organic form will also be constant, irrespective of the ratios. If, however, the ratio is altered with organic nitrogen, mineralisation of organic nitrogen may be the result. These require experimental investigation.

The third group comprises cultures containing only nitrate but no sugar. In this case, the changes in carbon and nitrogen are too small to be detected by the methods of analysis employed. The bacterial activity was probably at a minimum. Where, however, ammonium sulphate was substituted for sodium nitrate, there was a loss of about 10% in total nitrogen while the rest had been converted into nitrate nitrogen. Fixation of carbon might be expected in this case and by the 'addition of sugar nitrification might be impeded.

Under field conditions, there would be slow decomposition of nitrate in the presence of sunlight first into nitrite and then at an accelerated rate into the gaseous form. This process would be considerably accentuated in the presence of moisture approaching the saturation capacity of the soil.

A STUDY OF THE FLUCTUATIONS IN ORGANIC NITROGEN CONTENT OF BLACK COTTON SOIL UNDER VARYING CONDITIONS OF CROPPING.

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INTRODUCTION.

In a series of laboratory experiments on wheat soils from the north of the C.P., conducted some years ago, it was observed (Bal, 1927) that no appreciable fixation of nitrogen occurred in these soils when incubated for varying periods of 2 weeks to 6 months, with adequate moisture content, but without any addition of organic matter. Even if there was a very small amount of nitrogen fixed (0·001 to 0·002%) it would mean an addition of 20 to 40 lbs. of nitrogen per acre per year which would be more than enough for an average annual wheat crop from such soils. It was considered desirable to study the organic nitrogen content of black cotton soil under field conditions during different seasons and the effect of different crops on soil organic nitrogen. This paper records the results obtained in this connection.

Determination of organic nitrogen content of black cotton soil during
the period April to December.

In the first instance periodical determinations of organic nitrogen in unmanured black cotton soil, uncropped and cropped, were carried out for a period of nearly 7½ months from 16th April to 29th November. Uniform plots were selected on the Agricultural College Farm, Nagpur, and periodical soil samples were taken from these plots for purposes of analysis. Organic nitrogen in the various samples was determined by the modified Kjeldahl method, previously published by the writer (Bal, 1925), and the results obtained are given in Table I.

The results recorded in Table I show that the soil organic nitrogen fluctuates very considerably from time to time and that, both loss of nitrogen and re-cuperation of nitrogen appear to take place in the soil, under ordinary field conditions. These results are in accordance with the earlier observations recorded by Wilsdon and Barkatali (1922), and Lander and Barkatali (1925) in the case of Punjab soils and the recent observations of Sahasrabuddhe and Abhyankar (1936) in the case of soils from the Bombay Presidency. It will be observed that out of the total of 34 nitrogen estimations carried out,

TABLE I.

Variations of organic nitrogen in black cotton soil.

Time of sampling			Percentages of organic nitrogen in dry soil			
Month		Date	Unmanured and uncropped		Unmanured and cropped with gram	
			Actual	Average	Actual	Average
April	16	0·057 ⎱ 0·053 ⎰	0·055	0·054 ⎱ 0·060 ⎰	0·057
,, ...	30				
May	13	0·049 ⎫ 0·054 ⎬ 0·051 ⎭	0·051	0·054 ⎫ 0·056 ⎬ 0·057 ⎭	0·056
,, ...	21				
,, ...	24				
June	1	0·053 ⎫ 0·067 ⎪ 0·052 ⎬ 0·064 ⎪ 0·048 ⎭	0·057	0·054 ⎫ 0·055 ⎪ 0·052 ⎬ 0·055 ⎪ 0·050 ⎭	0·053
,, ...	4				
,, ...	9				
,, ...	16				
,, ...	30				
July	9	0·061 ⎫ 0·057 ⎪ 0·055 ⎬ 0·056 ⎪ 0·053 ⎭	0·056	0·055 ⎫ 0·056 ⎪ 0·052 ⎬ 0·052 ⎪ 0·051 ⎭	0·053
,, ...	14				
,, ...	19				
,, ...	24				
,, ...	29				
August	9	0·057 ⎫ 0·053 ⎬ 0·060 ⎪ 0·061 ⎭	0·058	0·050 ⎫ 0·049 ⎬ 0·048 ⎪ 0·053 ⎭	0·050
,, ...	14				
,, ...	19				
,, ...	24				
September . .	2	0·054 ⎫ 0·059 ⎪ 0·055 ⎬ 0·058 ⎪ 0·060 ⎭	0·057	0·049 ⎫ 0·052 ⎪ 0·052 ⎬ 0·051 ⎪ 0·058 ⎭	0·052
,, . .	8				
,, . .	16				
,, . .	22				
,, . .	28				
October	5	0·065 ⎫ 0·062 ⎪ 0·056 ⎬ 0·058 ⎭	0·060	0·053 ⎫ 0·048 ⎪ 0·052 ⎬ 0·050 ⎭	0·051
,, . .	13				
,, . .	21				
,, . .	28				
November . .	1	0·053 ⎫ 0·056 ⎪ 0·060 ⎪ 0·054 ⎬ 0·059 ⎪ 0·050 ⎭	0·055	0·064 ⎫ 0·066 ⎪ 0·052 ⎪ 0·061 ⎬ 0·066 ⎪ 0·048 ⎭	0·059
,, . .	10				
,, . .	13				
,, . .	15				
,, . .	24				
,, . .	29				

13 show a loss of nitrogen of more than 4% in the case of the uncropped plot, and 8 only in the case of the plot cropped with legume. Nitrogen content of the cropped plot rose up appreciably in the month of November. There was no definite indication of any particular periodical decrease or increase in

the nitrogen content of the soil due to season, during the period covered by the investigation.

Nitrogen fixation capacity of black cotton soil at different periods.

Samples of soil were taken from two experimental plots, one being kept fallow and the other being cropped with *Rabi* crops. Samples were taken at an interval of 10 days during the period—15th of May to 24th of November. Amount of nitrogen fixed in Ashby's mannite solution by the soil, representing the various samples, was determined in duplicate and the results obtained are recorded in Table 2.

TABLE 2.

Nitrogen fixed by one gram of soil per gram of mannite.

Month			Average amount of nitrogen fixed in milligrams after 14 days' incubation at room temperature (average of duplicate flasks)	
			Soil from the fallow plot	Soil from the cropped plot
May	..	..	..	10·50	9·80
June	..	..	..	9·75	8·72
July	..	..	..	9·94	9·19
August	..	..	..	8·68	8·44
September	..	..	..	9·19	8·40
October	..	..	..	8·75	8·26
November	..	..	..	9·03	8·26

The results given in Table 2 indicate a higher nitrogen fixation capacity of the fallow soil than that of the cropped soil. Periodicity in nitrogen fixation capacity is not well marked, as was observed by Walton (1915). Nitrogen fixation is, however, somewhat higher in the months of May, June and July than that in the months of August to November.

Effect of growing annually wheat and legumes, alone or in a mixture, on the nitrogen content of the black cotton soil.

With a view to determining the fluctuations in organic nitrogen content of the soil under controlled conditions, the following pot culture experiments were carried out for a period of nine years :—

A quantity of black cotton soil from the Agricultural College Farm, Nagpur, was obtained and was mixed very thoroughly and several samples of the mixed soil were taken for the determination of initial organic nitrogen present therein. The mixed soil, without any addition of organic manure

TABLE

Organic nitrogen in soil

No. of pots	Crops grown	1922 Initial at start	1923 Removed by crop	1923 Present in the soil	1924 Removed by crop	1924 Present in the soil	1925 Removed by crop	1925 Present in the soil	1926 Removed by crop	1926 Present in the soil
1 } 16	Uncropped ..	7·415	*nil*	7·576	*nil*	8·434	*nil*	9·065	*nil*	9·357
2 } 15	Wheat annually ..	7·415	0·042	7·592	0·023	7·926	0·023	9·190	0·024	8·721
3 } 14	Gram annually ..	7·415	0·138	7·909	0·634	8·537	0·119	9·467	0·041	9·201
4 } 13	Mixed wheat and gram annually.	7·415	0·106	7·852	0·133	8·076	0·095	9·533	0·088	8·915
5 } 12	Lakh annually ..	7·415	0·102	7·806	0·118	8·402	0·184	9·065	0·038	8·881
6 } 11	Mixed wheat and lakh annually.	7·415	0·068	7·996	0·092	8·171	0·187	8·673	0·081	9·775
7 } 10	Masur annually ..	7·415	0·022	7·782	0·141	8·100	0·272	8·900	0·157	8·994
8 } 9	Mixed wheat and masur annually.	7·415	0·035	7·569	0·088	8·123	0·152	8·737	0·092	8·978
	S.E.			0·216		0·245		0·287		0·366
	S.E.%			2·77		2·17		3·00		4·02

AVERAGE AMOUNT OF ORGANIC

III.

from various pots.

NITROGEN PER POT IN GRAMS

1927		1928		1929		1930		1931		Average of 9 years 1923–1931
Removed by crop	Present in the soil	Removed by crop	Present in the soil	Removed by crop	Present in the soil	Removed by crop	Present in the soil	Removed by crop	Present in the soil	
nil	9·538	*nil*	8·878	*nil*	10·000	*nil*	11·202	*nil*	9·758	9·313
0·045	9·490	0·044	8·680	0·028	9·610	0·013	11·114	0·004	9·840	9·128
0·048	10·220	0·157	9·348	0·075	9·850	0·073	11·175	0·059	11·030	9·622
0·082	9·551	0·121	9·004	0·080	10·172	0·087	10·811	0·055	10·830	9·421
0·072	9·744	0·131	9·316	0·092	9·704	0·140	11·256	0·085	11·590	9·528
0·113	9·909	0·112	9·530	0·105	10·087	0·126	11·350	0·109	11·060	9·613
0·145	9·475	0·023	9·617	0·109	9·800	0·113	10·582	0·051	11·010	9·362
0·102	9·640	0·053	8·362	0·094	9·363	0·061	10·348	0·059	10·490	9·066
	0·366 3·77		0·381 4·19		0·399 4·06		0·950 8·65		0·400 3·73	0·150 1·60

or fertilisers, was then filled in 16 pots of equal size. Thirty-five pounds of soil were added to each pot and crops were grown annually as required. A representative sample of the various types of seed used for sowing was analysed every year. The amount of nitrogen added to the soil by the seeds employed for sowing, the amount of nitrogen removed by the crop, and the amount of nitrogen left in the soil before subsequent crop was sown, were determined every year. In the case of the cropped pots either 10 plants of wheat only or 5 plants of wheat and 5 plants of the appropriate legume were grown as required.

The types of crops grown in the various pots and the results of annual determinations of nitrogen in the soil are given in Table 3. The results show the following :—

(1) The organic nitrogen content fluctuates from year to year. A remarkable increase in the nitrogen content of the soil from all the pots has occurred in the year 1930.

(2) The nitrogen content of the soil, at the close of the period of 9 years, is appreciably more than that initially present.

(3) Growing wheat annually for a period of 9 years does not appear to have caused any deterioration in soil organic nitrogen. At Rothamsted, in the case of the unmanured Broadbalk wheat plot, it was found that although there was a very little decrease in the actual nitrogen content of the soil after a period of 48 years, the nitrogen balance sheet drawn after taking into consideration the wheat crop obtained, showed a gain of one pound of nitrogen per acre per year (Russell, 1926).

(4) Growing a mixture of wheat and legumes annually does not show any significant increase in soil organic nitrogen over that found in the soil growing wheat alone.

The writer expresses his thanks to Dr. R. J. Kalamkar for having calculated the figures of standard error included in Table 3 and to Mr. R. N. Misra, Assistant to the Agricultural Chemist, for the help rendered by him in connection with some of the analyses of soils and crops.

SUMMARY.

(1) Results of (a) periodical determinations of organic nitrogen and nitrogen fixation capacity, in black cotton soil under field conditions, and (b) pot culture experiments conducted to study the effect of fallowing and cropping with various crops, on soil organic nitrogen, have been given.

(2) It has been observed that organic nitrogen in black cotton soil, under varying conditions of cropping, fluctuates very considerably from time to time.

(3) Under field conditions both loss of nitrogen and recuperation of nitrogen take place, but the latter process appears to be of a more frequent nature than the former.

(4) No definite indication of any periodical decrease or increase in the nitrogen content of the soil due to season was noticeable, but the nitrogen fixation power of the soil was found to be somewhat higher in the months of May, June and July, than that in the months of August to November.

(5) In the pot culture experiments conducted for a period of 9 years, it was observed that the nitrogen content of the soil from all the pots at the close of the experiment was appreciably more than that initially present, and in the year 1930 it had increased rather remarkably.

(6) Growing wheat annually for a period of 9 years has not caused any deterioration in soil organic nitrogen.

(7) Growing a mixture of wheat and legumes annually does not show any significant increase in soil organic nitrogen over that found in the soil growing wheat alone.

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SOME NEW ASPECTS OF THE MECHANISM OF NITROGEN FIXATION IN THE SOIL.

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During recent years a large volume of work has been directed towards the elucidation of the mechanism of non-symbiotic nitrogen fixation in the soil. These studies have been mostly carried out with pure strains of the genus *Azotobacter*. This is partly due to the historical association of those organisms and partly to their ability to fix fairly large amounts of nitrogen in the artificial media that are generally employed. On the other hand, very little information is available regarding the precise manner in which these organisms function in the soil; as to whether they stand competition with other organisms, and the extent to which the combined activities of all the organisms contribute towards nitrogen fixation in the soil.

Much valuable work has already been carried out on the nitrogen transformations attendant on fixation. Only meagre data are available, however, regarding the changes undergone by the carbonaceous materials which are utilised in the process, the nature of their degradation products and the manner in which they are transformed into the ultimate products of fixation. The relation of these products to the growth of the organisms and their ability to fix nitrogen are also awaiting solution.

It is well known that, under ordinary field conditions, there is comparatively very little fixation of atmospheric nitrogen; indeed, the various attempts that have been made during the past few decades to enrich the soil by artificial inoculation of *Azotobacter* and allied organisms have not proved very successful (Lipman, 1908; Bottomley, 1914; Emerson, 1918; Brown and Hart, 1925). On the other hand, Wilsdon and Barkat Ali (1922) and a·few other workers have reported considerable increase in the nitrogen contents of certain arid tracts which could be accounted for only by fixation from the atmosphere. Moreover, a number of workers have reported periodical increase in the nitrogen contents of soils (Sahasrabuddhe and co-workers, 1928, 1931, 1936; Annet *et al.*, 1928, and others) which cannot be entirely accounted for by non-biological transformations. These observations would suggest that, although, under normal conditions, the extent of fixation may be almost negligible, there are yet certain special conditions under which quite large quantities may be fixed. A fuller understanding of the foregoing and other observations will be possible only if the various factors influencing the efficiency of fixation in the soil can be satisfactorily determined.

With a view to throwing some light on these and allied problems, the present enquiry was undertaken.

<center>EXPERIMENTAL</center>

Previous studies on carbon transformations during fixation of nitrogen by *Azotobacter*, particularly by Stoklasa (1908), would suggest that organisms belonging to that genus derive their nutrition chiefly from carbohydrates. Working with *Azotobacter chroococcum*, Ranganathan and Norris (1927) observed that decomposition of sugar was comparatively slow ; that the fixation of nitrogen was complete before the entire quantity of sugar was used up. Regarding these observations, it is difficult to determine whether it was due to the slow action of *Azotobacter* or to the smallness of the inoculum. Moreover, as the sugar was present all through in the medium, it is not possible to ascertain whether any of the products of fermentation was utilised in the fixation of nitrogen.

The following experiments were therefore carried out with an active strain of *Azotobacter chroococcum*, Beij., isolated from the local soil. Heavy growths of the organism were obtained on Ashby's mannite agar medium using the cellophane technique of Bhaskaran *et al.* (1936). The growth (which was free from the solid medium) was shaken up with sterile water and the resulting suspension used for inoculation. The liquid medium used for the study was similar to Ashby's original composition with the difference that glucose was substituted for mannite. At stated intervals, the distribution of carbon and nitrogen in the medium was determined according to Bhaskaran and Subrahmanyan (1936).

<center>TABLE I.</center>

<center>*Distribution of Carbon.*</center>

Time in days	Organic carbon (in mg.) in 25 c.c. of medium				Lost as gas (mg. of carbon)
	Total	Present in slime and bact. cells	Present as sugar	Present in other soluble forms	
0	92·9	0·50	92·0	0·4	*nil*
3	88·7	9·8	70·1	8·8	4·2
6	76·0	10·5	64·9	....	16·9
10	48·0	12·0	28·7	7·3	44·9
14	30·0	15·7	*nil*	14·3	62·9
18	31·6	15·6	,,	16·0	....
22	22·1	16·1	,,	6·0	70·8
26	17·8	16·2	,,	1·6	75·1

TABLE II.

Distribution of Nitrogen.

Time in days	Nitrogen (in mg.) in 25 c.c. of medium			C-N ratio of slime and bact. cells
	Total	Present in slime and bact. cells	Present in the supernatant	
0	0·14	0·04	0·10	14·25
3	0·43	0·33	0·10	29·30
6	0·95	0·82	0·13	12·80
10	1·07	1·03	0·04	11·75
14	1·20	1·09	0·11	14·30
18	1·24	1·12	0·12	13·90
22	1·28	1·24	0·06	12·8
26	1·22	1·14	0·08	14·2

There was steady fall in the total organic carbon content of the medium. The sugar was used up in the course of 14 days, but considering the heaviness of the inoculum, the progress should be regarded as being comparatively slow. The decomposition proceeded very much more rapidly in presence of the mixed flora of the soil, the entire quantity of sugar being used up in the course of 4 days (*vide infra*). The major part of the sugar was converted into gaseous products, but a small part was also taken up by the organisms. The growth of the organisms came more or less to a stop after the sugar was used up. The residual organic matter is accounted for by certain water-soluble forms, chiefly organic acids (Ranganathan and Norris, *loc. cit.*). These forms increased up to a point but were then used up by the organisms. They did not contribute to the dry weight of the organisms but were converted into gaseous forms, chiefly carbon dioxide.

A comparison of the above with the distribution of nitrogen showed that the major part of the fixation took place before the sugar was entirely used up. The subsequent fixation was almost negligible, so that it may be concluded that the residual organic matter was not utilised in the fixation. The fixed nitrogen was mostly in the slime and in the bacterial cells, but a small portion was always left in the supernatant. The C-N ratio of the growth showed wide fluctuations in the early stages but attained a more or less steady value after the 14th day.

The foregoing observations would show clearly that fixation by *Azotobacter* is closely linked up with the availability of the carbohydrate. The residual organic matter was not utilised to any appreciable extent in the fixation.

The above results are supported by observations on the growth of the organisms and storage of organic carbon and nitrogen in the cells and slime.

TABLE III.

Growth in relation to fixation of carbon and nitrogen in cells and slime.

Time in days	Bacterial count in millions per c.c.	Dry matter of cells and slime (in mg.)[1]	Organic carbon of cells and slime (in mg.)	Organic nitrogen of cells and slime
0	61·0	2·4	0·5	0·04
3	90·1	25·3	9·8	0·33
6	151·3	36·0	10·5	0·82
10	....	38·0	12·0	1·03
14	190·5	36·6	15·7	1·09
18	192·5	38·6	15·6	1·12
22	181·0	36·5	16·1	1·12
26	....	39·7	16·2	1·14

A comparison with the previous tables would show that there was no increase in bacterial numbers after the disappearance of sugars : nor was there any appreciable increase in the dry matter, organic carbon or organic nitrogen content of the cells.

An entirely different set of results was obtained when the soil itself (representing the mixed flora) was used for inoculation into a similar medium.

TABLE IV.

Distribution of carbon.

Time in days	Organic carbon (in mg.) in 50 c.c. of medium.				Lost as gas (as mg. of carbon)
	Total	Present as sugar	Present in sediment [2]	Present in supernatant	
0	173·7	170·4	....	....	....
2	111·7	83·6	13·6	94·8	62·0
4	55·0	nil	24·2	27·5	118·0
8	53·4	....	39·8	10·3	120·3
12	52·5	....	39·9	9·3	121·2
16	50·5	....	39·4	7·8	123·2

[1] Correction has been made for the weight of unused calcium carbonate which separated with the organisms.

[2] The soil used for inoculation contained 3·3 mg. of carbon, but correction has been applied for this.

TABLE V.

Production and Distribution of organic acids.

Time in days	Organic acids (as mg. of c. in 50 c.c. of medium)						Total
	Non-volatile	Volatile					
	Lactic	Acetic	Propionic	Butyric	Total		
2	6·1	2·7	0·6	3·8	7·1		13·2
4	12·8	3·1	0·4	3·5	7·0		19·8
8	nil	. . . .	. . . .	. . . .	5·8		5·8
12	nil	. . . .	. . . .	. . . .	4·8		4·8

TABLE VI.

Distribution of Nitrogen.

Time in days	Nitrogen fixed (as mg.) in 50 c.c. of medium			C-N ratio of mucilage
	Total nitrogen	Nitrogen in sediment	Nitrogen in supernatant	
2	0·78	0·39	0·39	43·9
4	1·26	0·39	0·87	62·1
8	2·42	1·93	0·49	20·6
12	3·07	2·90	0·17	13·8
16	3·15	2·95	0·20	13·4

It may be seen that the sugar was decomposed at a very rapid rate, the entire quantity being used up within 4 days. Only less than a third of the organic carbon was left behind in the medium, the rest being lost as gas. The organic carbon in the supernatant was present mostly as acids (chiefly lactic acid), but this was used up between the 4th and 8th days for conversion into microbial tissue.

The study of the nitrogen transformations also showed that the fixation took place mostly between the 4th and 12th days, that is, after the sugar was entirely used up. A small quantity of nitrogen always remained in solution, but this bore no relation to the rate of fixation. The C-N ratio tended steadily to narrow down to a constant value.

These observations were supported by direct experiments with the soluble organic matter left after the disappearance of sugar. On being sterilised and then inoculated with the mixed flora, the soluble residues fixed nearly two-thirds as much nitrogen as the original sugar itself.

TABLE VII.

Fixation of Nitrogen by the water soluble residue left after decomposition of sugar.

Time in days	Nitrogen fixed (in mg.) by 50 c.c. of :	
	Filtrate sterilised and freshly inoculated	Original sugar medium
4	0·25	2·10
8	1·62	2·62

A further observation of interest was that the supernatant liquid (consisting chiefly of the mixed calcium salts of organic acids) was used up in the subsequent fixation. The solid sediment consisting of the living cells together with the insoluble products formed in the medium did not fix any appreciable quantity of nitrogen when left as such.

TABLE VIII.

Relative efficiencies of supernatant and sediment in fixing nitrogen.

Time in days	Nitrogen fixed (in mg.) in 50 c.c. of medium		
	Supernatant	Sediment	Unsterilised (control)
4	1·25	0·39	2·10
8	1·62	0·44	2·62
12	1·67	0·44	2·77

It would be seen from the foregoing, that, in presence of the mixed flora, the carbohydrate was extremely unstable and was rapidly destroyed. The products of decomposition, though small in quantity, were economically utilised in the fixation. These observations would suggest that if, by some means, the carbohydrates can first be converted into the mixed acid products before inoculation with the soil flora, then it may be possible to obtain greater return of fixed nitrogen for the carbon utilised than would otherwise be the case.

It has already been shown (Bhaskaran, 1936) that if the carbohydrate is first fermented under conditions of restricted air supply, then the major part of the organic carbon is converted into acid products. These can be neutralised with lime and utilised as their mixed calcium salts.

With a view to standardising the conditions for the application of the mixed calcium salts, some experiments were carried out substituting them for sugar in Ashby's medium. It was found that when they were used in fairly large quantities (on the same carbon basis as the original sugar), only a very small portion was used up. The corresponding fixation was also small, but the ratio of carbon utilised to nitrogen fixed was quite satisfactory, being of the order of 17 : 1. This would compare very favourably with the result obtained when sugar was used as the source of carbon. In the latter case, the ratio of carbon utilised to nitrogen fixed was of the order of 60 to 1 (Bhaskaran and Subrahmanyan, *loc. cit.*).

TABLE IX.

Effect of applying large quantities of mixed calcium salts.

Time in days	Total organic carbon (in mg.)	Total nitrogen (in mg.)
0	132	*nil*
4	120	0·42
8	115	0·95
12	106	1·50

The dilute residue left after fermentation of sugar was utilised to a greater extent than the concentrated product. There was also greater fixation of nitrogen, but the ratio of carbon utilised to nitrogen fixed was more or less the same as in the previous experiment. Combination of the mixed calcium

TABLE X.

Nitrogen fixation by the residue left after anaerobic decomposition of sugar.

Time in days	Total organic carbon (in mg.)	Total nitrogen (in mg.)
0	93	*nil*
4	82	0·70
8	58	1·54
12	55	2·06

salts together with the sugar did not lead to more economic fixation of nitrogen except when the quantity of the former was comparatively small.

TABLE XI.

Effect of combining sugar with the mixed calcium salts.—Changes in carbon.

Time in days	Organic carbon (in mg.)			
	Sugar solution alone (control)	Sugar solution +20 mg. equivalent of mixed calcium salts	Sugar solution +40 mg. equivalent of mixed calcium salts	Sugar solution +80 mg. equivalent of mixed calcium salts
0	100·2	120·2	140·2	180·2
4	97·0	118·5	137·7	170·0
8	48·8	84·0	98·8	103·0
12	47·0	66·8	75·5	86·4

TABLE XII.

Effect of combining sugar with the mixed calcium salts.—Changes in nitrogen.

Time in days	Total nitrogen (in mg.)			
	Sugar solution alone (control)	Sugar solution +20 mg. equivalent of mixed calcium salts	Sugar solution +40 mg. equivalent of mixed calcium salts	Sugar solution +80 mg. equivalent of mixed calcium salts
0	*nil*	*nil*	*nil*	*nil*
4	0·84	0·93	0·97	0·93
8	2·60	3·01	3·11	3·10
12	3·50	4·21	4·46	4·70

The concentrate added to the fermented medium after the sugar was entirely used up did not fix more nitrogen than that used as such, the ratio of nitrogen fixed to carbon utilised (1 : 20·6) being similar to that previously obtained.

TABLE XIII.

Effect of adding the acid concentrate after the sugar was used up.

Time in days	Organic carbon as mg. in 100 c.c. medium		Nitrogen fixed (in mg.) by the mixed calcium salts
	Sugar alone (control)	Sugar +20 mg. equivalent of mixed calcium salts	Experimental *minus* Control
0	28·4	48·7	*nil*
4	....	38·1	0·70
8	28·0	34·8	0·80
12	24·0	31·6	0·88

Experiments with two different types of soils (one a local specimen and the other an alkali soil from Sindh) showed that when the concentrate was applied at 20 mg. to every 10 g. of soil, the efficiency of fixation was of the same order as those previously reported.

TABLE XIV.

Fixation of nitrogen by the mixed calcium salts in different soils.

Time in days	Organic carbon (in mg.)		Nitrogen fixed (in mg.)	Ratio of nitrogen fixed to carbon utilised
	Soil (10 g.)+20 mg. equivalent of mixed calcium salts	Carbon utilised	Experimental *minus* Control	
Bangalore Soil				
0	70·5	*nil*	*nil*	. . . .
4	65·1	5·4	0·32	1 : 16·9
12	61·6	9·9	0·88	1 : 11·3
17	58·2	12·3	0·93	1 : 13·2
Kalar Soil				
0	69·0	*nil*	*nil*	. . . .
4	66·3	3·6	0·50	1 : 7·2
8	62·3	7·6	0·66	1 : 11·5
12	57·1	12·8	. . . .	. . . .
17	54·7	15·2	0·91	1 : 16·7

In both the cases, the untreated soil did not show any appreciable variation in organic carbon, so the corresponding figures have not been recorded.

During the first 4 days, the rate of fixation in the soil was very high, the ratio of nitrogen fixed to carbon utilised being as narrow as 1 : 7 in one of the soils. Although there was some slackening in the later stages, the final results should still be regarded as satisfactory.

The quantities of the mixed calcium salts added in the previous experiments would correspond, approximately, to 2 tons of organic carbon per acre. The nitrogen fixed by these would amount to about 2 cwts., i.e., about 13·5 cwts. of protein or about 2·5 tons of a good seed cake.

The recent work of Burk and Horner (1936) would suggest that the fixed nitrogen is easily assimilated by plants. The foregoing observations would show that the preparation of the mixed calcium salts from a cheap carbohydrate waste like molasses and its subsequent application to land would be an economical way of indirectly supplying a useful quantity of readily available nitrogen to the soil.

DISCUSSION.

Perhaps the most striking observation arising from the present enquiry is that the fixation of nitrogen by the mixed flora of the soil (which is the nearest approach to soil conditions) follows a different course from that of *Azotobacter* alone. The latter is comparatively slow in decomposing sugar. The fixation proceeds only as long as the sugar lasts : the residual organic matter is not utilised to any appreciable extent in the fixation. On the other hand, the mixed flora of the soil, though fewer in number, are extremely rapid in decomposing the sugar. Only a small quantity of nitrogen is fixed in presence of the sugar while the major part (amounting to over two-thirds of the total nitrogen) is fixed in the later stages. It has also been demonstrated that the products of decomposition of sugar, consisting chiefly of organic acids, are utilised in the subsequent fixation. These observations would suggest that, although *Azotobacter* may be potent by itself, it does not play any important part in presence of the other organisms of the soil. The latter decompose the sugar at a very rapid rate, so that, even if the *Azotobacter* is active in the soil, it will receive only a limited amount of organic nutrient and will, in consequence, fix only a small amount of nitrogen. Since *Azotobacter* does not utilise the residual organic matter to any appreciable extent, it has to be inferred that the fixation observed after the disappearance of sugar is presumably due to the agency of the other organisms of the soil.

It is well known that many of the soil organisms (other than those of the genus *Azotobacter*) are capable of fixing nitrogen. It is probable that some of them are active in the soil and are primarily responsible for the fixation consequent on the application of sugar. The nature of these active organisms and the manner in which they function are still obscure. Further work is to throw light on this aspect of the problem.

A further observation, which is also of considerable importance, is that the residue left after the decomposition of sugar is highly potent in fixing nitrogen in the soil. The return of nitrogen to carbon utilized is highly favourable (being under 1 : 20) and thus brings it to a high degree of efficiency which can stand comparison with those of the chemical and electrochemical methods now in vogue. The nitrogen thus fixed will be in organic combination and, being also readily available, will be very much more valuable than the inorganic forms that are now being manufactured.

The success of the new method of fixation would naturally depend on the availability of cheap sources of organic carbon and on the efficiency of conversion of the available forms into organic acids. Among the raw materials, molasses is one of the most abundant and is, at present, cheaply available. The conditions for the fermentation of molasses have already been standardised, rate of air supply being the most important factor. Under favourable conditions, 80–90 per cent of the total organic carbon can thus be converted into acids. The other sources of organic carbon would include the various

types of plant residues which can also be fermented, under similar conditions, to yield organic acids. Further work is needed, however, to standardise the conditions for the concentration of the acid products and their supply in a dry, non-hygroscopic form to the consumers. Work in this direction is in progress.

The nature of the components that are utilised in the fixation by the mixed flora of the soil is still obscure. It would be of considerable interest to determine the rates at which the different organic acids are being used up. The available evidence would suggest that lactic acid is being most readily utilised, but direct experiments with that acid, both in the free condition and as the calcium salt, would be needed before any conclusion can be drawn. There are also other components, organic as well as inorganic, which may play an important part in the fixation. Further studies on the mechanism of the related changes will not only throw more light on the problem but may also suggest new means of increasing the efficiency of fixation.

It has already been shown that the fixed nitrogen is readily available. Further work is, nevertheless, needed to determine whether it is available, with the same facility, to all types of crops and under different soil and climatic conditions. Vegetation experiments with the different types of crops are already in progress and it is hoped that, before long, it will be possible to throw some further light on this aspect of the problem.

SUMMARY.

Decomposition of sugars by even heavy inocula of *Azotobacter* proceeds comparatively slowly. After the sugar is entirely used up, there is very little growth of the organism : nor is there appreciable fixation of nitrogen. The residual organic matter is decomposed by the organism, but is not utilized in the fixation. These observations are supported by plate counts and the study of the distribution of organic carbon and nitrogen.

On the other hand, the mixed flora of the soil (though comparatively small in number to begin with) decompose the sugar at a very rapid rate, the entire quantity being destroyed in under 4 days. During this period, there is some growth of the organisms, but very little fixation of nitrogen. Between the 4th and 12th days, the residual matter, consisting chiefly of organic acids, is used up not only for the growth of the organisms but also for the fixation. These observations would show that the mechanism of fixation of nitrogen by *Azotobacter* is different from that by the mixed flora of the soil.

Direct experiments with the residue left after the decomposition of sugar showed that they were utilised by the soil flora in a more efficient manner than the original sugar itself. When left by themselves, these organisms showed no ability to fix nitrogen.

It has been shown that the mixed calcium salts of organic acids left after anaerobic decomposition of carbohydrates can be utilised in the fixation of

nitrogen. These products are decomposed comparatively slowly, but the return of nitrogen fixed for carbon utilised (under 1 : 20) is more than three times that obtained when the carbohydrate is applied directly to the soil.

The efficiency of fixation by the mixed calcium salts under different conditions has been studied. It has been found that the maximum fixation takes place when the concentrate is applied in quantities corresponding to about 2 tons of organic carbon per acre. The nitrogen fixed by this will be 2 cwts. and would correspond to 13·5 cwts. of protein, which, in turn, would be equivalent to 2·5 tons of a good seed-cake. The presence of sugar or other fermentable matter does not appreciably interfere with the fixation by the calcium salts. When applied in equivalent quantities, nearly the same amounts of nitrogen are fixed in different soils.

The practical significance of the foregoing and other observations and their application in field practice are indicated.

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A NEW ASPECT OF THE MECHANISM OF NITRIFICATION IN SOIL.

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One of the characteristic features about the classical nitrifying bacteria is their repugnance to organic substances. Indeed, the presence of more than traces of substances such as sugar or peptone entirely inhibits their growth and respiration. In apparent contrast to this, nitrification proceeds unimpaired in soil and sewage where there is a wealth of organic matter of animal and vegetable origin.

The apparent inconsistency in the behaviour of these organisms has been explained as being due to one or more of the following :—

(1) Omeliansky [1] (1899) has shown that, in combination with *Bacterium ramosus*, the nitrite-forming organism can grow, respire and cause the oxidation of ammonia even in dilute peptone broth (1 in 20). Ammonia is first produced and, after several days, nitrite appears. When in addition to these two bacteria, the nitrate former is inoculated in the dilute broth, nitrate is produced, but only after a month. It appears, therefore, that under conditions such as occur in nature, the growth and activity of the nitrite-forming bacteria are not interfered with by the presence of organic material.

Cutler and his associates (cf. Russell) [2,3,4] have recently described a number of species of bacteria which can produce nitrite from ammonia. These organisms were first found in the effluent from a beet sugar factory, and have since been shown to be widely distributed in the soil. They function in presence of organic matter and can withstand high acidity (pH 4·8). The quantities of ammonia nitrified by these organisms are however very small, the maximum amount of.nitrite nitrogen ever formed being only 3·2 parts per million. Even this tends to disappear in the later stages of the experiment. Under similar conditions, *Nitrosomonas* can produce much more nitrite (nearly a hundred times as much), so that the potential possibilities of the classical organisms under the soil conditions cannot be entirely ignored.

Barritt [5] (1933) has recently suggested that there is a possibility of the nitrifying bacteria being a phase in the life-cycle of heterotrophic organisms. This view of course vaguely questions the strict autotrophic character of the organisms tacitly assumed by Winogradsky and somewhat rigidly demonstrated by other workers. Readily assimilating carbonic acid, the organisms of nitrification appear as perfect autotrophs, the various attempts in proving them rather to be facultative heterotrophs having failed entirely.

No conclusive evidence regarding any of the foregoing suggestions is so far available. The question of the internal metabolism of the nitrifying bacteria has not yet been discussed. The synthesis of sugar and protein implies the existence of an enzyme system similar to that occurring in the protoplasm of plants. The writer has, however, shown[6] that the process of nitroso-fermentation is essentially a surface catalytic reaction and that there is no evidence to show that any one particular enzyme system is active in the process of nitrification.

Bonazzi[7] has suggested the possibility of carbon dioxide respiration of the autotrophic bacteria to account for nitrification in the absence of free carbon dioxide in nitrifying cultures, but since free carbon dioxide is not essential for the process, this is not evidence of katabolism, but in mixed cultures (as for example, cultures obtained in soil and sewage) the necessary carbon dioxide is obtainable from the normal respiration of the heterotrophic bacteria and it is possible therefore that there is a process of ' give and take ' between the organisms of the soil—in other words, some sort of ' Chemomixotrophic ' metabolism or ' symbiosis ' occurring in nature.

Starkey[8] observed that the nitrifying bacteria showed increased ability to oxidise ammonia in regions of maximum root development. He also found that there was close correlation between carbon dioxide production and abundance of microbial population. The profuse use of oxygen by the nitrifying bacteria is very well known and this, taken with the fact that adsorbed or condensed oxygen in soil has an unfavourable effect on the ordinary heterotrophic microflora of soil, points to a far reaching possibility that organisms in soil derive mutual benefit from one another in various ways.

With a view to throwing some light on this aspect of the problem, the present enquiry was undertaken. The procedure was to follow the oxidation of ammonia in presence of organic matter by the nitroso bacteria when acting alone or in conjunction with other organisms involved in the transformation of nitrogen in soil, e.g., *Bacterium mycoides*, *Bacterium megatherium*, two very important organisms of the ammonifying group, and *Azotobacter chroococcum*, a very important nitrogen fixing organism. In the case of *Azotobacter*, Barthel[9], and Kellermann and Smith[10] have definitely shown that the bacterial cells do not nitrify at all, and, as such, cannot produce nitrate in synthetic media. The experiments were made in purely liquid or soil cultures.

EXPERIMENTAL.

The bacterial strains used in this work[*] were freshly cultured in the respective media and incubated until vigorous growth was obtained. At this stage the colonies were picked by a sterile platinum loop and inoculated into

sterile water until a very strong suspension was obtained. This was carefully aerated with the necessary precautions and portions of this active suspension used for the experiments.

The Omeliansky medium was used as the source of ammonia for the organisms. Magnesium carbonate (2 per cent) was added to the medium except in cases when ammonium carbonate was substituted for the sulphate. An actively nitrifying culture of the nitroso organism was employed for these experiments. The study of nitrification consisted in following the course of the reaction by the Griess-Ilosvay colorimetric method and in certain cases by the method evolved by the writer[11]. The cultures were incubated at 30° and the nitrite formed was estimated from time to time.

I. *Nitrification of Omeliansky solution using mixed flora of soil as inoculum and the influence of glucose on the oxidation of ammonia.*

Fresh garden soil was used as the source of the mixed flora. Aliquots (50 c.c.) of Omeliansky medium were placed in several 250 c.c. Erlenmeyer flasks plugged with cotton wool and magnesium carbonate (separately sterilised ; 1g.) was added to each flask. Various concentrations of sterile glucose solution were added to several of the flasks followed by 5 c.c. portions of a suspension of fresh soil in distilled water. The volume of liquid in each flask was finally brought up to 100 c.c. by addition of requisite quantities of sterile water. Duplicates were run in all the cases and control cultures without treatment were also kept. Table I gives the results of these experiments, and Table II those of a study of the action of glucose on nitrification by a pure culture of the nitroso organism.

A comparison of the two sets of results will show that while glucose is toxic to the organisms oxidising ammonia to nitrite (*vide* Table II) when mixed flora of the soil are used instead of the pure culture, nitrification can go on even in presence of glucose so long as the concentrations are fairly low.

TABLE I.

Influence of glucose on nitrification by the mixed flora of the soil.

Days of incubation.	Nitrite nitrogen (in mg.) formed per litre.					
	Concentration of glucose (per cent).					
	0	0·025	0·05	0·075	0·1	0·2
0	Trace	Trace	Trace	Trace	Trace	Trace
7	,,	4·0	4·0	,,	,,	Nil
14	13·7	15·7	11·9	,,	,,	,,
21	29·4	36·0	33·4	7·9	5·3	,,
28	43·0	63·7	46·7	28·0	15·8	,,
40	65·9	88·9	70·0	36·0	20·0	,,

TABLE II.

Influence of glucose on nitrification by the nitroso bacteria.

Days of incubation.	Nitrite nitrogen (in mg.) formed per litre.					
	Concentration of glucose (per cent).					
	0	0·025	0·05	0·075	0·1	0·2
0	2·0	2·0	2·0	2·0	2·0	2·0
7	12·8	2·0	2·0	Trace	Nil	Nil
14	24·9	1·9	2·0	,,	,,	,,
21	49·0	5·5	,,	,,	,,	,,
28	66·0	7·6	,,	,,	,,	,,
40	87·0	13·0	Trace	,,	,,	,,
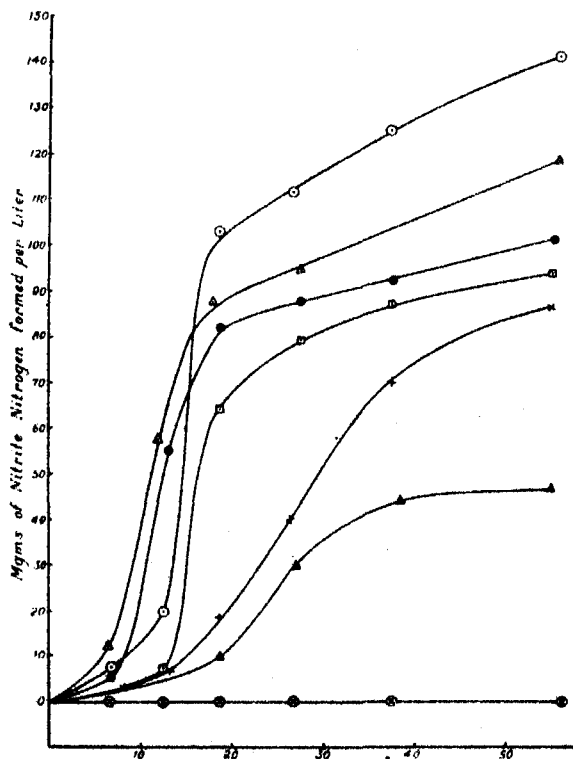
Fig. 1.　　　Time of observation in days.

○———○ Nitrosomonas + Azotobacter + glucose
▲———▲ 　　,,　　+ 　　,,　　(no glucose)
●———● 　　,,　　+ B.mycoides + glucose
◨———◧ 　　,,　　+ 　　,,　　(no glucose)
×———× Nitrosomonas alone
▲———▲ 　　,,　　+ glucose 0·1%
●———● B mycoides or Azotobacter alone

Fig. 2   Time of observation in days
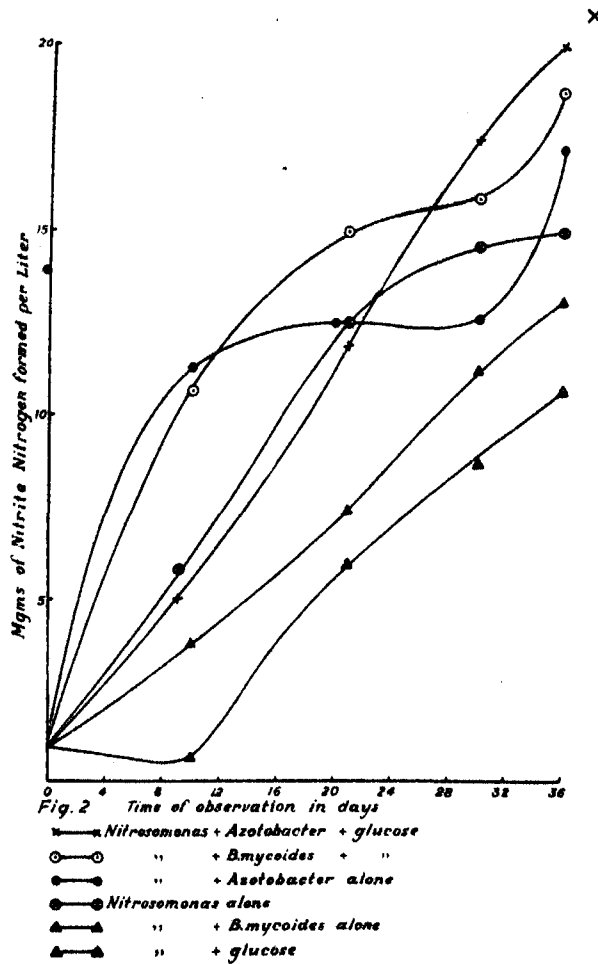
II. *Nitrification of Omeliansky medium by nitroso bacteria in presence of organic matter and the effect of mixed inoculations of the nitroso ferment with* Bacterium mycoides, Bacterium megatherium, *and* Azotobacter chroococcum *respectively.*

(1) *Glucose.*—The methods of culturing and study were exactly as detailed above. Thick bacterial suspension (2 c.c.) was used for inoculation in each case. The results are represented in Fig. I. The concentration of glucose used was 0·1 per cent. It is known that nitrification is inhibited by a glucose concentration of 0·025 to 0·05 per cent and completely checked by glucose concentration of 0·2 per cent in pure cultures.

These results show that whenever *Nitrosomonas* was accompanied by other strains of organisms, glucose did not depress nitrification ; on the other hand, in several cases, nitrification was enhanced. Fig. II represents the results of a similar study in soil cultures. 100 gram portions of a local specimen of soil (powdered to pass through a 30 mesh sieve) were employed for each culture together with 1 to 2 gms. of calcium carbonate. The samples were sterilized and 20 c.c. of sterile Omeliansky medium added to each culture. They were then inoculated with the different organisms, the details of procedure being the same as outlined above. The results show that there is very striking parallelism between nitrification as obtained in liquid cultures and that in soil cultures.

There was no nitrification when *Bacterium mycoides* or *Azotobacter* was inoculated into soil cultures in the absence of nitrite formers.

(II) *Humic acid.*—Since humic acid is one of the most important soil constituents, it was considered desirable to study nitrification by mixed cultures in presence of this substance. Humic acid used in this study was prepared according to Burk *et al*[12]. The requisite quantity was weighed into each culture flask and sterilised and then sterile media added. The results are given in Table III.

The nitrifiers used in these experiments were very active. It may be added that natural humic acid (freshly prepared) and a specimen of humic acid from Messrs. E. Merck (Dramstadt) exhibited no fundamental difference in their influence on nitrification. The natural product showed a higher nitrification in all the cases.

It may be seen that at very low concentration (0·025 per cent) humic acid stimulates nitrification. As the concentration increases, there is a steady fall in efficiency until, at about 0·5 per cent, there is practically no nitrification.

When *Azotobacter chroococcum* or *B. mycoides* is combined with the nitrifying organism, a different type of result is obtained. There is no stimulation at low concentrations of humic acid, but the adverse effect of the higher concentrations is not so pronounced as when the nitrifying organism functions alone.

(III) *Peptone.*—Increasing concentrations of peptone retard nitrification. There is marked depression at 0·25 per cent while at 1 per cent there is no nitrification for over 6 weeks. Results are given in Table IV. The adverse effect is not appreciably removed by combining the nitrifying organism with *Bacterium mycoides*, but there is slight improvement in presence of *Azotobacter chroococcum*.

No nitrification was observed in cultures inoculated with *B. mycoides* or *Azotobacter* alone into sterile medium with and without peptone.

Preliminary experiments have shown that in the presence of very dilute solutions of nutrient broth nitrification takes place when inoculated with a combination of the nitrifying bacteria with *B. mycoides* or *Azotobacter.*

TABLE III.

Influence of Humic acid on Nitrite forming bacteria when present alone and when in mixed cultures.

NITRITE NITROGEN (in mg.) FORMED PER LITRE.

Days of observation.	Nitroso Bacteria alone. Concentration of Humic acid (per cent)						Nitroso Bacteria + Azotobacter chroococcum Concentration of Humic acid (per cent)					Nitroso Bacteria + Bacterium mycoides Concentration of Humic acid (per cent)				
	0	0·025	0·05	0·1	0·2	0·5	0·025	0·05	0·1	0·2	0·5	0·025	0·05	0·1	0·2	0·5
0	2·6	2·6	2·6	2·6	2·6	2·6	2·6	2·6	2·6	2·6	2·6	2·6	2·6	2·6	2·6	2·6
10	62	120	40·4	25·5	14·6	3·9	45·0	70	17·0	2·8	5·7	4·7	16·8	24·7	18·6	14
20	104·7	128	107	98·3	14·6	3·9	76·2	115	29·0	3·8	30	4·7	22·4	87·5	65	53
32	125·8	132·5	114·2	100	14·6	3·9	108·7	119	53·3	43·1	35	4·7	83·6	97·4	70	53
60	170·0	199	126	112	14·6	3·9	121·8	140	88	45·0	49·0	5·2	93·3	131·8	74	55
90	207·4	213	172	133	14·6	3·9	160	180	104	48·0	55·0	37·3	142	132	74	56
114	229	239	182	118	22·4	4·0	187	182	110	50·0	60·0	94·5	146	132	70	47

TABLE IV.

Nitrification of Omelianský medium in presence of peptone by the nitrite forming bacteria when acting alone and when in presence of mixed cultures.

NITRITE NITROGEN (in mg.) FORMED PER LITRE.

Concentration of Peptone (per cent).

Days of incubation	Nitroso bacteria alone				Nitroso bacteria + *Bacterium mycoides*				Nitroso bacteria + *Azotobacter chroococcum*			
	0·0 (control)	0·25	0·5	1·0	0·0 (control)	0·25	0·5	1·0	0·0 (control)	0·25	0·5	1·0
0	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
14	4·5	7·0	1·12	Nil	31·0	13	3·2	Nil	30	28	20	Nil
21	15·6	11·0	1·12	..	80·0	48	5·5	..	83	69	39	..
36	88·0	30·0	1·12	..	98·0	69	8·4	..	100	74	48	..
48	112·0	55·0	1·12	..	120·0	86	10·4	..	123	100	60	..
60	162·3	90·7	1·12	..	154·0	91·4	53	..	149	112	60	..
72	172·4	114	..	..	159·0	100	75	5·9	155	112	70	14
90	186·7	118	..	..	162·0	112	76	21·6	180	127	87	56
114	188	114	..	..	160·0	112	79	32	188	130	86	68

DISCUSSION.

The most striking observation that arises from the present enquiry is that the nitrifying organisms, which, by themselves, are strict autotrophs can, under certain conditions, not only tolerate organic matter but also function actively in its presence. This apparently inconsistent behaviour is due to the presence of the other organisms of the soil.

The manner in which the individual organisms that were experimented with, or the combined flora of the soil, facilitate nitrification cannot yet be adequately explained. It may be pointed out, however, that the commoner saphrophytes destroy sugars and other forms of fermentable organic matter, so that, by removing such undesirable constituents, they would be indirectly assisting the nitrifying organisms.

It has been observed that nitrification is stimulated by similar organisms even in presence of sugar. Although the available data are insufficient to explain this phenomenon, it may yet be observed that the classical nitrifying organisms are more potent in the soil than their behaviour in pure cultures would suggest.

Peptone inhibits nitrification, but its adverse effect may not persist long in the soil. It undergoes rapid ammonification by the other organisms of the soil and thus indirectly provides material for further nitrification.

Further work is required to elucidate the precise manner in which the interfering organic substances are destroyed by the mixed flora of the soil ; whether the immediate products of decomposition are so inimical to nitrification as the original substances. Information is also needed regarding the nature of the relation between nitrifiers and the other organisms of the soil ; as to how the latter stimulate nitrification, especially in presence of organic substances. These and allied problems are under investigation and will form the subjects of later communications.

SUMMARY.

(1) Nitrification by *Nitrosomonas* is inhibited by even very low concentrations (0·025 per cent) of glucose. On the other hand, in presence of the mixed flora of the soil, nitrification proceeds even at much higher concentrations (0·1 per cent) of sugar.

(2) When combined with *B. mycoides*, *B. megatherium* or *Azotobacter chroococcum*, *Nitrosomonas* functions actively even in presence of sugar. In some cases, the nitrification proceeded even to a greater extent than in presence of *Nitrosomonas* alone.

(3) When present in more than minute quantities, humic acid does not interfere with nitrification. Peptone has an adverse effect at concentrations of 0·25 per cent and above. In both the cases, the inhibitory action is mitigated by the presence of other organisms in association with *Nitrosomonas*.

(4) The mechanism of the related processes has been discussed. Evidence has been adduced to show that *Nitrosomonas* and the other organisms of the soil function in close association. Fermentable organic matter is rapidly destroyed by the saphrophytes of the soil thus leaving the conditions favourable to nitrification. The presence of the other organisms also helps the nitrifiers to tolerate certain forms of organic matter commonly present in the soil.

My sincere thanks are due to Prof. V. Subrahmanyan for his very kind interest in this work and helpful criticism.

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NITROGEN STATUS OF INDIAN SOILS.

By T. J. MIRCHANDANI, *Agricultural Chemist, Bihar.*

(Read at Symposium, August 29-30, 1936.)

The nitrogen content of most Indian soils varies from 0·03 to 0·07 per cent as against 0·10 to 0·17 per cent of European and American soils. This low level of nitrogen reflects itself in the yield of our staple crops. The nitrogen in the soil exists almost entirely in a combined form and the problem of nitrogen is therefore intimately connected with the organic matter of the soil. The study of the problem divides itself into three main divisions : (1) Increasing the store of nitrogen by a system of rotation of crops, by the addition of nitrogenous fertilisers or by fixation ; (2) the prevention of loss of nitrogen, and (3) utilisation of nitrogen by the crops. In fact, any system of land husbandry that has not as its aim these three objects in view is bound to fail.

1. *Increasing the store of nitrogen.*—A leguminous crop fixes the atmospheric nitrogen in addition to the supply of organic matter to the soil. Where this cannot be done, the land is usually fallowed, but this system has only a limited value because there is no addition of organic matter but only a small increase of nitrogen. Where neither of these processes are adopted the land is likely to deteriorate in its fertility unless heavily manured from time to time. Under irrigated condition the intensity of cropping can be as high as 80%, thus allowing no time for fallow. In such systems green manuring is an absolute necessity, especially when the supply of F.Y.M. is limited.

It is now generally accepted that for Indian soils at least the addition of inorganic nitrogenous fertilisers alone is not desirable, even though such treatment of the soil may immediately show an increased crop return. Continued application of artificial fertilisers has a deleterious effect on the soil and, as has been more recently shown, on the quality of the crops. The Department of Agriculture in Bihar, as I expect in many other parts of India, does not recommend artificials, except in combination with organic manures. When there is sufficient carbon, especially in the form of easily decomposing substances, the organisms thriving on their energy materials utilise all the nitrogen they get from the soil and fix some from the atmosphere. The utility of the organic fertilisers is therefore enhanced by the fact that they serve as a means to obtain nitrogen from the atmosphere. One instance of this may be mentioned here. Molasses, which is a waste product of the sugar industry, contains 0·3-0·5 per cent nitrogen and over 20% carbon. The sugar content is 45-60 per cent. When quantities varying from 250 mds. to 1,000 mds. per acre are added to the soil under laboratory conditions, there is found to be an increase in the total nitrogen content of the soil,

which is more than the nitrogen supplied by the molasses.　Table 1 illustrates this.

TABLE 1.

Nitrogen in milligrammes per 100 grammes of soil.

	Original.	One month incubation.	Two months incubation.	Three months incubation.	Four months incubation.
Soil alone	72·8	73·7	66·4	62·0	56·3
„ plus 1% molasses	77·2	77·6	83·5	66·0	64·8
„ „ 3% „	86·0	85·7	90·0	70·0	66·3
„ „ 4% „	90·4	92·6	99·4	82·0	69·1
„ „ 5% „	94·8	94·2	94·2	85·1	71·9

NOTE.—1% molasses corresponds to 250 mds. per acre and an increase of 1 mgm. per 100 gms. of soil equals 20 lbs. of nitrogen per acre.

Though the increase of 4–9 mgms. per 100 gms. of soil is definite in two months, the subsequent loss should be noted and an attempt made to prevent it.　The reason for this loss is not far to seek.　Experiments at Sabour have shown that on incubation, the oxidation of carbon in the molasses amounts to nearly 60% of carbon, which escapes as carbon dioxide in 30 days.　As soon as the carbon is lost, there is nothing to hold the nitrogen back.　But if the crops were growing on the land, the nitrogen will be utilised and not lost.　Great care is therefore necessary to arrive at an optimum period when the molasses should be incorporated in the soil, prior to putting the land to crop.　If the period is too short, a state of nitrogen starvation would be experienced by the growing plant as all the available nitrogen would be locked up by the soil micro-organisms ; on the other hand, if the period is too long, the danger of nitrogen loss exists.　A period of 4–8 weeks appears to be the optimum period.　It may happen that the period recommended may offer, in some instances, practical difficulties in farming, in which case it may be worthwhile ploughing in, after about one month, a less easily decomposing material such as straw to hold the nitrogen back.　The nature and amount of this material must depend upon the period that the molasses has to remain in the soil, before the crop is put in.　Experiments on this point are being carried out by me at Sabour.

What is true of molasses holds equally true for other organic manures. Another very useful manure is the habitation manure.　In trying out the Indore process of compost making in some of our trials, we composted sugar-cane trash and other farm residues with soil and got a perfectly good manure, giving a nitrogen content of 0·9 to 1·8%, depending upon the nature of the starting material, the highest nitrogen content having been obtained when sugar-cane trash alone was used.　The crop tests on wheat and maize in the pots showed that this manure can be used with advantage.　Table 2 illustrates this.

TABLE 2.

Yield of grain and straw in gms. per pot.

	Wheat.		Maize.	
	Grain.	Straw.	Grain.	Straw.
Control	43·69	56·7	18·0	23·0
F.Y.M. (40 lbs. N. per acre) ..	42·70	42·4	31·81	28·4
Habitation manure (40 lbs. N. per acre)	51·01	61·0	27·47	29·9

The residual value of this manure after the wheat crop is being investigated. This offers a cheap and good substitute for organic manures as it is only the waste products that are utilised in the preparation of this manure.

Oil cakes are also useful but their utility is limited by the fact that they leave very little humus in the soil.

2. *Prevention of loss of nitrogen.*—Nitrogen can either be lost as free nitrogen from the soil, as a result of denitrification, or as soluble nitrogen compounds in drainage. There is also a possibility of nitrogen loss as ammonia. The first and last processes are experienced only under few or specialised conditions and the loss is usually not considerable. There is, however, a large amount of nitrogen lost by drainage, if care is not taken in the methods of farming. One of the main causes of the loss is that the nitrogen gets too easily nitrified in the season when the crop on the land cannot utilise it fully, and it may be completely lost in drainage water. In one experiment, I found that the yield of the wheat crop was lower in the green manured plot than in the unmanured one. It looked paradoxical but subsequent investigation showed that the green crop (vetches) decomposed far too quickly, with the inevitable loss of nitrogen as nitrates. The extent of loss was measured and successful experiments done to prevent loss of nitrogen, by incorporating a cellulosic material like wheat straw to hold the nitrogen back. The results are shown below :—

TABLE 3.

	Nitrogen (milligrammes) per pot removed by leaching.
Soil alone	71·6
„ plus green manure	89·8
„ „ „ „ plus straw	46·4

It is desirable therefore to study in detail the nature of the manure that is applied to the soil. In the case of green crop, the age and season have a great deal to do with the rate of decomposition, the younger plants decomposing much quicker than older ones and the whole thing being greatly influenced by the moisture and aeration in the soil. The same thing holds for other types of organic matter.

3. *Utilisation of nitrogen.*—The final arbitrator of the value of the nitrogen is the plant and our present knowledge is that it takes up nitrates

most easily and ammonia in certain cases. It has also been suggested that the plant utilises simple forms of amino compounds, but the experimental evidence is by no means conclusive. The question of availability of nitrogen needs to be kept in the forefront, in considering the nitrogen status of Indian soils.

The decomposition of organic matter is the necessary preliminary to the release of plant nutrients in the soil, particularly nitrogen. It is now possible to give a quantitative measure of the effect of varying C : N ratio of organic manures on the course of their decomposition. The narrower the ratio, the quicker would be the decomposition. In many of my experiments a close relationship existed between the rate of decomposition and the C : N ratio of the decomposing material and it was possible to regulate the course of decomposition by artificially altering the C : N ratio of the substance. Two instances are quoted below. Activated sludge having C : N of 12 was used as a manure in pots and in the laboratory to study the rate of nitrification. To this was added varying quantities of cellulosic material to slow down its decomposition. The nitrogen level of the individual substance as well as the mixtures was kept the same, i.e. 5 mgms. of nitrogen per 100 gms. of soil. On the other hand, mustard plant, having a C : N of 26 and therefore very slow to decompose, was treated with small quantities of dried blood, keeping the nitrogen level the same, i.e. only altering the carbon level. The results are shown in the following table.

TABLE 4.

Ammonia and nitrate nitrogen in mgms. per 100 gms. of soil.

A.	2 weeks.	4 weeks.	7 weeks.	9 weeks.	14 weeks.	
1. Soil alone	1·14	1·73	0·93	1·36	1·30	
2. „ plus sludge	2·26	2·00	2·43	2·40	3·08	
3. Soil plus sludge plus 5% N. as straw	0·70	0·86	0·11	0·70	1·09	
4. Soil plus sludge plus 20% N. as straw	0·44	0·17	0·11	0·11	0·12	

B.	1 week.	3 weeks.	8 weeks.	18 weeks.	26 weeks.	34 weeks.
1. Soil alone	1·89	2·34	2·40	3·61	4·00	3·52
2. „ plus mustard	1·02	0·99	2·07	2·98	4·67	4·88
3. „ „ „ plus dried blood	1·34	2·18	3·63	4·70	6·27	7·33

In the case of sludge, the nitrogen is almost completely rendered unavailable when 20% of its nitrogen is replaced by straw giving the same quantity of nitrogen. In the case of mustard the quickening of the decomposition is evident from the data. Another interesting thing that emerges from the figures is that after nearly six months the nitrogen of the mustard is higher than that of the control, an observation which lends support to the view that the nitrogen, locked up by the soil micro-organisms, is released when the carbon and nitrogen have reached an equilibrium. After this there

would be a constant supply of available nitrogen for the plant. This was confirmed by the pot experiments.

Similar results were obtained when F.Y.M. was treated with straw and with dried blood to widen and narrow down respectively its C : N ratio.

The availability of nitrogen from organic manure is dependent upon the level of carbon existing along with it. It is necessary to stress this point, so that the value of the organic matter as a source of nitrogen should be assessed in its proper perspective. It is admittedly true, and my experiments have confirmed it, that the form in which carbon exists has a great deal to do with its power of regulating the nitrogen availability from a manure, but total carbon gives an approximate measure, in many instances a correct measure, of its effect on the decomposition of the organic matter.

A passing reference may be made to the importance of the time when nitrogen is available for the growing plant. From the manures having a wide C : N, the nitrogen would be available rather late and this would explain the failure of certain organic manures to give increased yields. If the availability is long delayed, the crop would not derive any benefit from such organic manure, in fact a state of nitrogen deficiency would be set up ; but the nitrogen made available about the flowering time of cereal crops goes to increase the protein content of the grain. Regulated nitrification thus provides a means of either increasing the yield or improving the quality of grain crops. This has been found to be correct in some of my experiments. Further work is in progress.

Summary.—The nitrogen level of Indian soils is low and it is essential to conserve, increase and profitably utilise the nitrogen of the soil. Addition of green manures, organic manures and the proper understanding of the mechanism of the decomposition of the organic matter to prevent losses and to utilise the nitrogen to best advantage, i.e. improving the yield and quality of crops are suggested so that further deterioration may not take place in the level of soil fertility.

A NOTE ON THE NITROGEN SUPPLY OF RICE SOILS.

By P. K. DE, *Agricultural Chemistry Section, Dacca University.*

(*Read at Symposium, August 29-30, 1936.*)

It is the experience of every cultivator of Bengal that, even in absence of any manure, rice can grow in the same field year after year, without causing any depletion in the fertility of the soils. Howard (1924) stated that in Bengal and in Burma large rice crops have been grown on the same land year after year for centuries, yet no change in the fertility of the soils has been observed. So far as the supplies of nutrients like phosphate, potash, etc. are concerned, crops may find them in the soils in amounts to meet their requirements over long periods. But as regards nitrogen, the supply of this element in the soil is relatively poor specially in Indian soils. It, therefore, becomes a matter of surprise how rice could get the large supply of nitrogen that was required for its growth over centuries. It suggests itself that atmospheric nitrogen is rendered available to the plant by some natural process. This can be done in two different ways : nitrogen may be fixed in the soils by some non-symbiotic processes and subsequently made available to the plants, or the plants them-selves may assimilate atmospheric nitrogen, like legumes. At present we do not know of any plant other than legumes, which has been definitely shown to possess the power of assimilating elementary nitrogen, though several workers have claimed to have been able to grow some non-legumes in absence of nitrogen. Rice never suffers from nitrogen deficiency, and the possibility of the fixation of nitrogen by this crop deserves very careful examination. In this connection it is noteworthy that Sen (1929) has demonstrated the occurrence of a nitrogen-fixing organism within the rice root, while Viswanath (1932) obtained indications that rice may assimilate atmospheric nitrogen.

A detailed investigation on the nitrogen supply of rice was started in this laboratory in 1931. It is not possible to give within the scope of this note a complete account of the results obtained so far and the details of experiments or of the references relating to different subjects. A brief account of the more important results and the conclusions they led to has been given in this note.

Fixation of nitrogen in the rice soils under water-logged conditions.[1]

The abundant growth of algæ in the submerged rice soils and the claims that certain algæ are capable of fixing atmospheric nitrogen, either independently or working in symbiosis with the nitrogen-fixing bacteria, suggest that some fixation may take place during the period the soil remains water-logged.

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[1] A paper embodying the results of this investigation has been communicated for publication in the *Indian Journal of Agricultural Science.*

As a result of extensive experiments, it is now definitely known that nitrogen is fixed in the rice soils during the period of water-logging. The results in Table 1 show that soils slightly alkaline in reaction fix much more nitrogen than those with lower P_H. In the former soils, abundant growth of algæ took place but in the latter the growth was much poorer. The addition of calcium carbonate to the latter soils, however, stimulated both algal growth and nitrogen-fixation (Table 2).

TABLE 1.

Fixation of nitrogen under water-logged conditions.

P_H of the soil.	N fixed, as p.p.m.
8·2	333
8·4	330
8·1	275
7·7	112
7·6	98
5·1	79
4·9	41
4·9	11

TABLE 2.

Effect of $CaCO_3$ on the fixation of nitrogen.

	N fixed, as p.p.m.	
P_H	Without lime.	With lime.
4·9	41	116
4·9	11	142
6·2	149	205
5·1	79	138

It has been shown that the fixation of nitrogen in the water-logged soils is not a bacterial process but an algal one. But the fact whether algæ themselves fix nitrogen or whether they do so in symbiosis with other organisms remains undetermined for the present. The following species of algæ were identified by Professor F. E. Fritsch, F.R.S., from the nitrogen-fixing cultures isolated from Faridpur soil :—*Plectonema notatum* Schmidle, *Phormidium orientale, Anabœna sphœrica* and an undeterminable green unicellular alga.

Fixation of nitrogen in the rice soils under dry conditions.

During the few winter months, the condition of the soils both as regards temperature and moisture are eminently suitable for the growth of *Azotobacter* and other aerobic nitrogen-fixing bacteria. Some fixation of nitrogen may, therefore, take place during this period. Experiments, however, showed that although fixation of nitrogen took place in some of the soils, yet by no means can it be regarded to be as general as the fixation under water-logged conditions. There were even losses of nitrogen from some soils, specially when they were treated with straw. The most interesting result in this connection is that considerable fixation was observed in some soils which did not contain *Azotobacter*. This led to a search for new nitrogen-fixing organisms

in the rice soils and as a result four different species of organisms (probably belonging to the genus *Azotobacter*) were isolated in pure conditions. These organisms were characterised by their slow growth in the nitrogen free mannite medium, large slime formation, non-motility and the absence of pigment formation.

Fixation of nitrogen by the rice plant.

Rice plants were grown on purified sand in glazed pots watered with a nitrogen-free nutrient solution. Though the plants were never so healthy as in the fields, yet they grew up to maturity with tillers and grain formation. A carefully prepared nitrogen balance-sheet showed considerable increase of this element (Table 3). The experiment was repeated in the following year and the previous observation confirmed (Table 4) :—

TABLE 3.

Sand culture experiments on the growth of rice plants in absence of combined nitrogen. (1933).

N as mgm.

Pot	Treatment	Total N at start in sand and in seeds sown	Residual N in sand after the experiment	Nitrogen in the crop			Total nitrogen recovered	Grain
				Straw	Root	Grain		
1	Uncropped	118·5	120·4	...	...	...	120·4	1·9
2	Cropped	119·8	139·5	12	7·6	20·4	179·5	59·7
3	,,	119·8	114·6	16·9	11·3	17·4	160·2	33·7
4	,,	119·8	116·8	20·2	10·8	10·3	158·1	31.3

TABLE 4. (1934).

1	Uncropped	114·6	118·5	...	...	...	118·5	3·9
2	,,	114·6	119·6	...	...	...	119·6	4·3
3	Cropped	116·3	107·0	24·8	8·7	15·5	156·0	39·7
4	,,	116·3	110·8	22·7	6·9	15·0	155·4	39·1
5	,,	116·3	105·1	16·9	7·0	14·1	143·1	26·1
6	,,	129·8*	109·9	18·4	5·6	10·8	144·7	14·9
7	,,	129·8*	114·6	44·8	12·5	23·7	195·6	65·8

In both sets of experiments, the nitrogen in the sand after the experiment remained practically unchanged. This indicated that the increase is due to the plants themselves. To ascertain whether the plants can assimilate elementary nitrogen without the help of other organisms, sterilised seeds were sown over pure quartz sand in wide test tubes, watered with sterile nitrogen-free nutrient solution, and constantly aerated with air passing through a number of sterile cotton plugs. The plants did not grow well under these conditions and their nitrogen contents were not significantly greater than those added with

* Treated with 13·5 mgm. of N added as KNO_3.

seeds. This suggests the inability on the part of the rice plant to assimilate nitrogen directly. In an attempt to discover whether there is a symbiotic relation between rice plants and any other nitrogen-fixing organism, it was observed that one or more nitrogen-fixing organisms exist within rice leaves. Small pieces of rice leaves were inoculated into a nitrogen-free cane sugar solution containing the necessary minerals. Growth took place and the determination of nitrogen after 3 weeks showed an average fixation of 2 mg. of nitrogen. A large number of leaves were examined in different periods of growth, in different seasons and from different localities. Fixation took place in every case. This shows that these organisms are the normal inhabitants of rice leaves and not contaminants or occasionals. Growth was observed also on silica plate inpregnated with cane sugar mineral solution, when inoculated with small pieces of rice leaves.
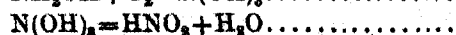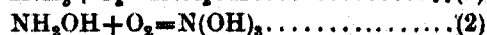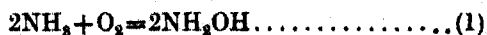
TABLE 5.

Mgm. of nitrogen fixed in 100 c.c. of the medium when inoculated with weak growths of ' leaf' bacteria.

1	..	..	·98	
2	..	..	·84	
3	..	..	·98	Mean 1·12 mg.
4	..	..	1·26	
5	..	..	1·4	

Loss of nitrogen from water-logged soils.

Investigation on the loss of nitrogen from water-logged soils showed that from unmanured soils little nitrogen is lost in the drainage, but from the soils treated with different organic manures the loss is considerable. Nitrogen is lost from the manured soils in the form of ammonia, non-amino nitrogen compound and humin nitrogen (nitrogen precipitated with MgO). Though a certain amount of nitrogen is lost in the gaseous form, particularly from soils of low nitrifying capacity, it is very small in comparison with the heavy loss brought about by bio-chemical processes. As early as 1913, Harrison and Aiyar demonstrated the evolution of elementary nitrogen from water-logged soils. No explanation has been given as to how elementary nitrogen can be evolved as a result of the decomposition of soil organic matter. The present investigation showed that this loss is not due to the decomposition of ammonium nitrite (Table 6). But it has been found that the loss takes place when the oxidation of ammonia begins. Evidences have been obtained in support of the following reaction :—

In normal dry soils the oxidation of ammonia takes place in the following way—(Corbet, *Biochem. J.*, 1935) :—

$$2NH_3 + O_2 = 2NH_2OH \ldots \ldots \ldots \ldots \ldots (1)$$
$$NH_2OH + O_2 = N(OH)_3 \ldots \ldots \ldots \ldots \ldots (2)$$
$$N(OH)_3 = HNO_2 + H_2O \ldots \ldots \ldots \ldots \ldots$$

In water-logged soils, the supply of oxygen is much limited. The reaction (2) therefore takes place in the following way :—

$$4NH_2OH + O_2 = 2N_2 + 6H_2O \ldots \ldots \ldots (3)$$

TABLE 6.

Decomposition of ammonium nitrite in water-logged soils.

Period of exposure to sun		Total N at start	N recovered as ammonia and nitrite	Total N recovered	Loss
24-5-36 to 13-6-36	..	19·35 (Quartz flask and sterilised).	6·3 *	18·48	·87
,, ,, ,,	..	19·35 (Jena flask and unsterilised).	nil	17·36	1·99
22-6-36 to 4-7-36	..	15·96 (Quartz flask).	5·32*	14·84	1·12
,, ,, ,,	..	15·96 (Jena flask).	3·92*	15·33	·63

In the first soil (P_H 4·9), the amount at start 19·35 mg. includes 5·49 mg. of N added as ammonium nitrite (sodium nitrite and ammonium chloride in equivalent amount).

In the second soil (P_H 8·1), 6·37 mg. of N were added as ammonium nitrite.

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* Includes a little organic nitrogen as the estimations were made by distilling soil with Devarda's alloy and magnesium oxide.

SEWAGE AS A SOURCE OF NITROGEN SUPPLY TO THE SOIL.

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(Read at Symposium, August 29-30, 1936.)

Sewage is one of the most potent sources of nitrogen supply to the soil. Its application to land would be not only an economical method of disposal, but also an elegant means of returning to the soil the major part of the fertilising ingredients originally removed from it in the form of crops. There are, no doubt, several problems, agricultural as well as hygienic, connected with sewage farming, but these do not justify the enormous waste that is going on. It is, indeed, distressing to find that the major part of the world's sewage is either thrown away—discharged into the rivers or the sea—, or, if applied to land, managed so uneconomically that the maximum benefit is rarely ever attained. In the latter case, there are the additional dangers of water pollution, soil sickness and the production of unhealthy crops through profuse application of undiluted sewage. In view of these, it has been considered desirable to make a critical study of some of the problems relating to sewage farming, especially in India, and to suggest means of improvement.

In many parts of India, only the kitchen waste passes into the sewers, while night-soil, which is generally collected by hand, is disposed off separately. It is only very rarely that industrial wastes (such as those from dye-house, tannery, or brewery) get admixed with sewage so that the special problems connected with their application to land do not generally arise.

The composition of raw sewage is variable, depending on the density of population, the nature of the wastes that find their way to the sewers, the available water supply, the conditions of the sewers and such other factors. The following results (Table I) will illustrate the above.

TABLE I.

Composition of different sewages : parts per 100,000.

Origin	Suspended solids	Ammoniacal nitrogen	Albuminoid nitrogen	Oxygen absorbed in 4 hrs.	Chlorine
Indian.					
Dacca*	12·5	5·0	0·24	3·6	9·6
Bombay (Matunga)* ..	31·8	1·08	1·62	..	3·36
Calcutta (Sibpur)* ..	25·6	0·17	0·02	7·1	17·0
Jamahedpur*	..	1·88	1·98	11·3	3·5
Madras*	..	3·3	1·26	7·6	17·5

* Cited from Swaminathan, *Jour. Indian Inst. Sci.*, 1929, **12A**, 139.

TABLE I—*continued*.

Origin			Suspended solids	Ammonia-cal nitrogen	Albuminoid nitrogen	Oxygen absorbed in 4 hrs.	Chlorine
English.							
Saltley*	..	..	57·7	4·06	1·52	26·3	18·9
Reading*	..	..	34·2	10·4	1·48	8·8	10·1
Sheffield*	..	..	77·4	5·09	1·22	13·9	..
Manchester (Davyhulme)*	..		17·8	2·32	0·76	7·2	10·8
American.							
Milwaukee*	..	..	25·9	1·56	0·89	12·5	19·4
Boston†	..	..	13·5	1·14	0·91	5·6	..
Chicago†	..	..	14·1	0·88	0·76	3·8	4·0

* Cited from Swaminathan, *Jour. Indian Inst. Sci.*, 1929, **12A**, 139.

† Cited from Kershaw, Sewage purification and disposal, 1925.

It may be noted that the English sewage is richer in nitrogenous constituents than the average Indian sewage. This is traceable to a number of factors, the most important of which are (*a*) the richness of the food consumed by, at any rate, a large section of the people and (*b*) inclusion of night-soil which is richer in nitrogenous constituents than ordinary kitchen waste. The dilute condition of the American sewage is accounted for by the liberal supply of water (some times as much as 200 gallons a day per head) in many of their cities.

There is periodical fluctuation in the composition of sewage (raw or treated) in any locality depending largely on the time of day or season of the year. The following observations relating to two important nitrogenous constituents will illustrate the possible extent of variation in one locality.

TABLE II.

Periodic fluctuations in the Ammonia and Albuminoid nitrogen contents of raw sewage, septic tank effluent and A.S. tank effluent : as parts per 100,000 of N.

Item		Raw Sewage	Septic tank effluent	A.S. tank effluent
Ammonia (free and saline)	..	1·68–3·25	1·8–3·3	0·51–0·76
Albuminoid nitrogen	..	0·69–0·89	1·14–1·54	0·12–0·15

These figures relate to the installation at the Indian Institute of Science.

The greater concentration is generally observed during the hot and dry months of the year. That also happens to be the season when liberal watering

is needed by market garden and other crops which are generally raised on sewage. This important fact has to be taken into account when considering the effect of prolonged application of undiluted sewage on agricultural crops.

The changes in composition are not, however, very considerable when the samples are collected over only a limited period and the daily collections are mixed together prior to application to land. The following observations relate to the effluent from one of the septic tank installations at the Indian Institute of Science.

TABLE III.

Weekly changes in the composition of septic tank effluent used for irrigation.
Parts per 100,000.

Weeks	Total solids	Chlorine	Ammonia-cal N.	Albumi-noid N.	Nitrite N.	Nitrate N.	Total N.
0	42·0	5·7	3·3	0·6	0·8	2·5	7·4
1	45·5	5·5	3·2	0·5	0·8	2·4	7·2
2	48·2	5·6	2·6	0·5	0·7	2·4	6·5
3	62·0	5·7	2·4	0·6	0·7	2·5	6·5
4	59·4	5·7	3·1	0·4	0·9	2·6	7·5
5	62·2	5·6	2·4	0·4	0·2	3·0	6·9
6	62·4	5·5	3·3	0·5	0·09	2·4	6·5
7	48·2	5·6	3·2	0·5	0·06	2·7	6·8
8	66·2	4·6	3·1	0·6	0·09	2·7	6·8
9	56·8	5·5	2·2	0·6	0·08	3·2	6·4
10	58·8	5·7	2·1	0·4	0·06	2·8	5·8
11	61·4	5·6	2·0	0·6	0·04	3·7	6·6
12	56·6	4·3	1·8	0·5	0·02	2·4	5·1
13	58·4	5·6	2·1	0·6	0·04	2·2	5·2
14	48·6	5·4	2·0	0·4	0·06	2·5	5·5
15	49·2	5·6	2·8	0·6	0·04	2·3	6·0
16	50·1	5·4	2·4	0·5	0·04	2·4	5·9

On application to land, all types of sewage undergo oxidation, yielding first ammonia and then nitrate. The rate of such oxidation is determined by various factors—the nature of the soil, the concentration of sewage, the efficiency of the previous treatment, especially in regard to removal of albuminoids, the manner and rate of application to land, cultivation operations, and such like. It may be stated, in general, that light soils are more efficient than heavy ones. Pre-treatment, especially that involving aeration, facilitates subsequent oxidation in the soil. Application in small instalments at a time and uniform spreading over land leads to quicker transformations than heavy or uneven, applications. Cultivation operations improve the rate of oxidation. If the applications are heavy and are continued indefinitely, the rate of oxidation tends to slacken. Even the best soils turn steadily sewage sick. There is multiplication of pathogenic and putrefactive organisms and the soil becomes smelly. In many cases there is fly and mosquito breeding and the

soil gets infected with hookworm. The standing crops, if any, show the effect
of adverse soil conditions. The plants get diseased and the yield is considerably
depressed. Such soils are generally inadequately drained and any effluent
that may pass out becomes a source of pollution to the water supplies in the
neighbourhood. It would thus be seen that sewage-sick soil is undesirable
not only from the agricultural point of view, but also from considerations of
public health. It is extremely important, therefore, that the oxidising efficiency
of the soil should be maintained and sewage sickness carefully avoided.

There is fairly extensive literature on the subject of sewage sickness,
but the available biochemical data are still not sufficient to show the precise
nature of the agents or the products responsible for the various phenomena
which have been reported. Furthermore, it is not very clear whether sewage
sickness is exclusively responsible for the abnormalities observed in the case
of certain crops which are raised on sewage. Some crops seem to tolerate
even fairly high concentrations of raw sewage whereas others suffer considerably
even if moderate quantities are applied. A useful amount of information
in this direction has been accumulated by a number of workers in different
parts of the world. Among the Indian stations, particular mention should
be made of the Hadapsar Farm near Poona and the Sewage Farm at Jamshed-
pur. The experience of the Poona workers, as also that of ours, have shown
that it is not desirable to apply sewage (especially in the raw condition) as such
to the soil. Many agricultural crops show undesirable effects (though the soil is
itself not apparently sick), which are traceable to excessive supply of certain
constituents, especially nitrogen. Suitable dilution of sewage (so as to contain
between 0·5 and 1·0 of total nitrogen part per 100,000) removed these undesir-
able effects. This, combined with proper cultivation operations and periodic
fallowing, should render sewage irrigation suitable for practically all types of
crops. In our experience, the effluent from the septic tank has to be diluted
three to five times if consistently beneficial effect is to be attained. The activ-
ated sludge effluent is reasonably safe during certain months of the year
(especially when there are periodical rains to effect the necessary dilution), but
even that has to be diluted with two or three times its volume of water if
it is to be freely used in all seasons of the year and for a variety of crops.

A few towns in India possess storm water tanks, which are generally
situated near the Sewage Works, the water of which can be used for suitably
diluting the sewage used for irrigation. When this facility is not available
and the soil is of the heavy type, the crops have to be chosen carefully for,
otherwise, many of them may fail altogether.

An alternative procedure for controlling the concentration of sewage
effluent used for irrigation would be that of adopting a suitable system of pre-
treatment which will not only remove the suspended matter but also retain
a considerable part of the soluble nitrogen in the form of sludge. None of
the present systems of sewage treatment is entirely satisfactory, however,
from this point of view. The septic tank effluent contains a large amount

of the nitrogen in ammoniacal form : albuminoids ammonify in the tank and thus increase the ammonia content of the effluent. The activated sludge process is highly efficient in holding up albuminoids which are clotted out in the form of sludge, but even that cannot retain nitrates and the small quantities of ammonia which may escape oxidation. The nitrate content of the effluent would depend partly on the ammonia content of the original sewage and as the average Indian sewage undergoes considerable amount of septic action (in the drains) before reaching the final disposal stage, it may be reasonably expected that it will contain considerable quantities of ammonia which will nitrify in the activated sludge tank and thus pass into the effluent. The other methods of sewage disposal are more or less intermediary in character between the septic tank and the activated sludge systems and will discharge a portion of the soluble nitrogen (partly as ammonia and partly as nitrate) into the effluent. In some cases, other forms of non-protein nitrogen may also pass into the effluent.

It has been shown by Richards and Weekes (*Proc. Inst. Civil Eng.*, 1921) that if sewage is passed over straw filters, a considerable part of the soluble nitrogen is held up by the straw. Straw filters are highly useful in a small way, but are rather inconvenient to handle when dealing with large quantities of sewage. Moreover, the straw loses its efficiency after some time and has to be replaced by a fresh lot. Furthermore, straw filters will not find favour in India because almost every kind of straw fetches a useful price as dry fodder for cattle. The experience with straw suggested, however, that there may be other cellulosic materials, which are at present going to waste and which can be utilised either by themselves or in association with some other system of sewage treatment for adsorbing the soluble nitrogen of sewage. Some encouraging results in this direction have been obtained by Messrs. S. Rajagopal and M. S. Muthuswami Iyer in these laboratories who have shown that if any powdered, cellulosic material is stirred up with raw sewage and the suspension aerated, not only the suspended matter but also the soluble nitrogen are taken up by the sludge. The resulting sludge settles down fairly easily and, under ordinary conditions, dries rapidly without giving any offensive odour. The modified procedure thus offers considerable practical possibilities and deserves to be tried out on a large scale.

It is well known that dilution of sewage is of assistance not merely in reducing the concentration of nitrogen but also in facilitating biological oxidations, thus leading to destruction of organic matter which would otherwise prove offensive. Ammonia is oxidised to nitrite and nitrate and the quantity of albuminoids considerably reduced. These effects are best seen when the diluted sewage is run for some distance in open channels prior to application to land. The effect of mere dilution is illustrated by the following results which were obtained with septic tank effluent at the Institute. The experiments were carried out with different proportions of water to effluent, but for the sake of convenience only one set of results have been cited.

TABLE IV.

Effect of dilution on nitrogen transformations in septic tank effluent.
Parts per 100,000.

Time in days	No Dilution				Diluted with 5 times its volume of water			
	Ammo-niacal N.	Albumi-noid N.	Nitrite N.	Nitrate N.	Ammoni-acal N.	Albumi-noid N.	Nitrite N.	Nitrate N.
0	7·1	0·8	0·0	0·0	1·02	0·10	traces	0·02
1	6·3	0·7	0·0	0·0	0·93	0·11	0·02	0·028
2	6·5	0·6	traces	0·0	0·83	0·08	0·05	0·033
3	6·3	0·4	0·06	0·0	0·55	0·07	0·04	0·030
4	6·2	0·5	0·1	0·0	0·50	0·07	0·05	0·066
5	7·1	0·5	0·1	0·0	0·38	0·07	0·66	0·066
6	7·1	0·4	0·1	0·0	0·25	0·05	0·72	0·043
7	6·7	0·3	0·07	0·0	0·20	0·03	0·70	0·04

The above results show only the effect of allowing diluted effluent to stand for some time. The oxidation will be more complete and the nitrite converted almost entirely into nitrate when the diluted effluent is applied to land.

TABLE V.

Ammonification and Nitrification in soil irrigated with diluted septic tank effluent.
Nitrogen in parts per 100,000.

Time in weeks	Ammoniacal N.	Nitrite N.	Nitrate N.
0	0·014	0·00	0·002
2	0·12	0·002	4·1
4	0·97	0·002	5·8
6	1·01	0·003	6·1
8	1·80	0·003	7·2

In the above experiments diluted sewage was applied to uncropped soil. It may be seen that the ammoniacal nitrogen shows a slight increase. Nitrite nitrogen is either absent or present only in traces. Nitrate nitrogen shows a steady increase and is, in fact, the chief product of oxidation of sewage in the soil.

If the diluted sewage is applied to soil under crop, there is very little accumulation of nitrate. This observation has been verified by trials with a number of crops, but the following results relate to only three of the crops which were watered with diluted septic tank effluent.

TABLE VI.

Distribution of nitrogen in sewaged soil under crop.
Nitrogen in parts per 100,000.

Time in weeks	SOIL UNDER RAGI			SOIL UNDER DOLICHOS LABLAB			SOIL UNDER TOMATO		
	Ammo-niacal	Nitrite	Nitrate	Ammo-niacal	Ni-trite	Ni-trate	Ammo-niacal	Ni-trite	Ni-trate
0	0·02	0·01	0·05	0·02	0·02	0·03	0·06	0·01	0·08
2	0·4	0·02	0·6	0·4	0·03	0·8	0·9	0·04	0·9
4	0·6	0·03	1·1	0·7	0·04	0·9	0·8	0·04	0·9
6	0·9	0·02	0·8	0·8	0·04	0·7	0·8	0·03	0·8
8	1·2	0·04	0·7	0·8	0·02	1·1	1·0	0·05	1·1
10	0·6	0·03	0·9	0·9	0·03	0·3	0·9	0·04	0·9
12	0·8	0·03	1·8	0·7	0·03	0·8	0·9	0·03	0·8
14	1·6	0·04	0·96	1·1	0·04	1·2	1·1	0·03	0·8
16	1·2	0·04	1·4	0·9	0·04	0·9	0·8	0·04	1·2

It may be mentioned that the ammoniacal nitrogen remains more or less at the same level as in uncropped soil. Nitrite is present only in traces. Nitrates are used up nearly as fast as they are produced.

Mineral fertilisers like superphosphate or potash (if applied in moderate quantities) have no influence on the oxidation changes. On the other hand, they stimulate plant growth and thus indirectly facilitate increased intake of nitrogen. The nature of the crop (and especially its root system) is also an important factor determining the active concentration of nitrogen left in the soil. It may be stated generally that grasses and other dense crops not only tolerate fairly high concentrations of sewage nitrogen but also utilise it nearly as fast as it is applied.

Yield of crops raised on diluted sewage effluent.—All the commoner agricultural and market garden crops can be raised successfully on diluted sewage. It is difficult to prescribe any single formula for the dilution as it will depend largely on the strength of the original sewage and the pretreatment received by it. With the septic tank effluent of the composition given in Table III, dilution with three times the volume of water has been found to be most satisfactory. The diluted sewage can be applied to almost any crop with consistently satisfactory results. In the case of some crops, there is delayed ripening of grains but this can be overcome by either reducing the volume of sewage or further increasing the dilution until the approach of the harvest period.

Elephant grass.—The experiments were conducted on small plots laid out on a uniform area of land. One set of plots was watered while the other received diluted sewage. Four plots were allotted to each treatment. The plots were distributed at random. The cuttings were taken just before flowering and the yields have been presented in Table VII.

TABLE VII.

Effect of sewage irrigation on yield of elephant grass—successive cuttings

(Area, 400 sq. ft.)

Date of harvest			YIELD IN KILOGRAMS	
			Sewage irrigated	Water irrigated
6th June	..	..	102·4	46·0
11th July	..	..	206·8	101·7
7th August	..	..	210·6	115·5
5th October	..	..	222·3	141·2
23rd November	..	..	92·2	66·9
8th January	..	..	68·2	43·4
11th February	..	..	46·8	19·5
25th March	..	..	93·4	36·3
28th May	..	..	291·1	91·3
13th July	..	..	302·6	154·3
4th October	..	..	213·9	146·5
22nd November	..	..	121·0	89·3

The yields from individual cuttings have been considerably modified by the season, the wet months (July to October) being generally more favourable than the dry ones (December to April). The effect of season was of more or less the same order in both the sets and it may be seen that the sewaged plants did consistently better than the watered ones.

Lucerne.—The experimental details were similar to those in the case of elephant grass. The yields (Table VIII) show a striking difference between sewage and water irrigation.

TABLE VIII.

Effect of sewage irrigation on yield of lucerne—successive cuttings.

Date of harvest	YIELD IN KG.		Date of harvest	YIELD IN KG.	
	Sewage irrigated	Water irrigated		Sewage irrigated	Water irrigated
15th May	31·3	16·8	26th March	25·5	9·1
12th June	21·8	11·6	10th April	26·1	8·3
8th July	18·8	9·3	30th April	15·3	5·9
6th August	24·8	14·0	16th May	14·3	5·4
22nd August	21·5	13·9	5th June	11·1	4·4
12th September	22·3	10·3	23rd June	15·4	4·9
7th October	31·9	16·1	17th July	24·7	6·2
1st November	41·0	18·3	2nd August	31·7	8·3
28th November	35·5	17·9	25th August	24·6	6·7
16th December	40·3	17·5	11th September	25·7	6·6
7th January	36·2	15·4	3rd October	29·1	7·7
27th January	33·9	13·0	23rd October	23·9	7·7
18th February	35·4	13·5	15th November	25·3	8·0
6th March	35·6	11·7			

It may be observed that while the watered plants tended steadily to deteriorate with time, the effect was not so prominent in the case of the sewaged ones. Lucerne also shows the effect of season, but not so pronouncedly as elephant grass.

Grain and Market garden crops.—These experiments were conducted in pots. The pots were divided into two sets, one receiving basal dressing of superphosphate and the other left untreated as control.

Of these, again, one half was watered with diluted sludge and the other with tap water. The results have been given in Table IX.

TABLE IX.

Yield of grain and market garden crops (pot expts.).

Crop			YIELD PER POT (IN G.) AFTER TREATMENT WITH			
			Super followed by sewage	Sewage alone	Super followed by water	Water alone
Barley	..	..	51	42	8	6
Tomato	..	..	1,400	1,390	508	175
Peas	..	..	38	34	17	15
Dolichos	..	..	431	175	149	70
Potato	..	..	300	167	117	100

It may be noted that barley responds very well to sewage, the yield being more than five times that in the watered control. Basal dressing with superphosphate leads to further increase in yield. The effect on tomato is also striking, the sewaged plants being vastly superior to the watered ones. The effect of super is, however, more pronounced in the case of the watered plants than in that of the sewaged ones. Peas have also responded well to sewage, but the effect is not so striking as in the case of other crops. Dolichos and potato have both done well on sewage, but in their case the effect of super is even more striking. This is particularly noticeable in the case of sewaged plants.

Other Crops.—These experiments were carried out in plots, the conditions being similar to those described previously (Table X). The total yields of elephant grass and lucerne from the respective plots have also been included.

<div align="center">TABLE X.</div>

Yield of grain, market garden and fodder crops (in plots)

Crop	YIELD (IN KG.) AFTER TREATMENT WITH—	
	Sewage irrigated	Water irrigated
Maize	15·6	10·8
Radish	135·6	71·6
Carrots	80·6	31·2
Elephant grass (13 Cuttings) ..	1454·8	750·9
Lucerne (27 Cuttings)	723·0	288·5

It may be observed that in all the cases the sewaged crops gave much higher yields than the watered ones. The most striking response was from lucerne and carrots, the sewaged plots yielding nearly thrice as much as the watered ones.

Manurial value of sewage sludges.—Pre-treatment of sewage involving the separation of sludge offers an additional advantage in that the sludge can be used as a fertiliser. The sludge may be separated by chemical pre-cipitation, intensive aeration or mechanical agitation. Any two or all the three types of treatments may also be combined into one system. Prolonged septic action also yields a sludge but the product is generally very small in quantity as compared with those obtained by other methods. All these sludges have only limited application when present in the wet condition and tend to revert on standing. They are also inconvenient to handle, so they are not of much commercial value unless they can be properly dried.

Several methods have been proposed for the drying of sewage sludge. Most of them are comparatively expensive. The most efficient are those involving the filtration of sludge from the adhering water followed by machine drying. These involve costly outfit and are not suitable except on a very large scale. The recently introduced Fowler mat is exceedingly simple in design and is, at the same time, highly efficient as a filter unit. It yields a spadeable sludge which can be dried on the mat itself or by any one of the other methods. The mat sludge can also be easily dried in the sun.

Some experiments were carried out at Bangalore, comparing the manurial values of sewage sludges obtained by different methods. Starting from the same type of raw sewage, sludges were obtained after intense or limited aeration, chemical precipitation by different methods or prolonged septic action. Among these, the product obtained after intensive aeration was the most satisfactory. It kept after some time and offered no difficulty in filtration. The dried pro-duct obtained from it was the richest (3·5 to 4 per cent) in nitrogen. Re-

duced aeration yielded a slightly smelly product which did not keep well even for a few hours. It also offered difficulty in filtration. The dried product was comparatively poor in nitrogen (2·5 to 3·0 per cent). This was traceable to the fact that the sludge receiving limited air supply had very poor clotting action, so that a part of the nitrogen was allowed to pass into the effluent.

The results obtained by chemical precipitation (by ferric or aluminium sulphate) were nearly similar to those after limited aeration, except that the filtration was slightly easier. On the other hand, the sludge was bulky and the dried product poor in nitrogen. There was very poor yield of sludge after prolonged septic action. The dried product contained larger quantities of mineral (soil) matter and was the poorest in nitrogen (1·5 to 2·0 per cent). Both from the point of view of quality and quantity, the septic tank sludge (which would correspond in some respects to the residue left after digestion for gas) is rather poor and cannot be regarded as possessing any high manurial value.

When applied on equivalent nitrogen basis, sewage sludges were generally found to be superior to inorganic fertilisers. The following results (Table XI) obtained at Bangalore with three different types of crops will illustrate the above.

TABLE XI.

Manurial value of Sewage Sludge (Pot expts.).

Treatment	YIELD (IN G.)			
	Lucerne	Potato	Ragi	
			Grain	Straw
No manure (control)	704	400	9	22
Super alone	1,772	250	12	31
Nitrate alone	805	270	10	26
Nitrate *plus* Super	1,687	410	16	37
Chemically precipitated sludge ..	2,871	990	39	110
Chemically precipitated sludge *plus* Super	3,373	1,000	40	111
Activated sludge	4,983	1,130	..	..
Activated sludge *plus* Super ..	4,283	1,160	37	109

Lucerne showed better response to super than to nitrate. Chemically precipitated sludge yielded better and activated sludge the best. Addition of super proved useful in the case of the chemically precipitated sludge, but there was evidence of depression when combined with activated sludge. The response of potato was similar to that of lucerne though not so striking. The yields of ragi were also of the same order except that the chemically precipitated sludge was nearly as effective as activated sludge. This may be due to the fact that ragi is a crop of fairly long duration (six months), so that both

the types of sludges would have had sufficient time to undergo the necessary decomposition in the soil.

Physiology of crops raised on sludge.—There is comparatively scanty literature on this important aspect of sewage farming. Most of the available records relate to the abnormalities observed when undiluted sewage is persistently applied for watering crops. Under such conditions, crop lodging is often observed. In many cases the adverse effects are not seen till a late stage. The leaves get crinkled and, in some cases, there is practically no flowering or seeding. Many of the crops also get diseased, stem and root rots being the most common. Insect attacks of various types have also been reported.

The researches carried out by S. A. Rafay at the Indian Institute of Science with a variety of crops showed that the crops raised on diluted sewage exhibit none of the above-mentioned abnormalities. The plants come out quite healthy. The vegetative growth is of the same type as that obtained with a liberal supply of a nitrogenous fertiliser. The leaf area is increased and the shoot height distinctly improved. There is also greater tillering, the number of tillers in sewaged plants being about 50 per cent more than the watered controls. Flowering and seeding are favoured with attendant improvement in yields. There is delayed ripening in some cases, but this can be largely overcome by suitable basal dressing of superphosphate.

Crops that respond most favourably to sewage treatment.—This observation would apply primarily to sewage farms which have no facilities for either dilution or otherwise reducing the concentration of nitrogen in the effluent. The crops have to be carefully chosen and planted in the right season, for, otherwise, they may fail altogether. The experience on the Bangalore farm during the past fourteen years would show that grasses (of different varieties), lucerne, cholam (fodder), plantains, papaya and cocoanut do fairly well even on undiluted sewage, at any rate, for a few seasons. Among the market garden crops, cabbage, cauliflower, tomatoes, lettuce, amaranthus and such like respond favourably. Certain creepers such as pumpkin, snake-gourd and cucumber also do well, at any rate, in most seasons. On the other hand, brinjals, chillies, lady's-finger, peas and most grain crops are very erratic in their response. In certain seasons they do well, while in others they fail completely. It is generally difficult to predict the results and considering that the failures are more numerous than the successes it would be advisable to leave out such crops altogether. Among the fruit trees, apples, oranges, and limes did not do well on sewage. Guavas and figs did somewhat better, but the results were not, on the whole, very satisfactory.

Quality of crops raised on sewage.—Attention has already been drawn to the fact that crops—especially those of the market garden type—raised on sewage do not keep well. It may also be added that in certain localities—especially if the drainage is unsatisfactory—they also smell of sewage. Certain sections of consumers have complained of inferior taste but the majority

cannot distinguish between the taste of vegetables raised on sewage and those on water.

Hygienic aspects of Sewage Farming.—The available evidence would suggest that suitably diluted sewage undergoes complete oxidation in the soil, so that it is hardly likely that it will be a source of pollution. The same cannot be said, however, of undiluted sewage, especially when the application is prolonged. The effluent draining out of the soil will not be a completely oxidised product and will be a source of pollution to unprotected water supplies in the neighbourhood.

In addition to the above, sewage contains a large amount of insect life, which is not destroyed except during prolonged septic action or intense aeration. If raw or incompletely treated sewage is applied to land, these are released and become a source of danger to crops as well as to public health. Separation of sludge—by one of the known methods—followed by its drying or digestion for gas is the most satisfactory way of eliminating insect pests.

Even under the most favourable conditions (including proper dilution), it may be reasonably expected that market garden crops raised on sewage will get polluted, at least mechanically, in the process of watering. Proper washing (preferably with a dilute solution of permanganate) followed by cooking (involving frying or prolonged boiling) will, no doubt, kill out a large part of the associated putrefactive organisms, but these operations are not and cannot ordinarily be carried out quite thoroughly even in the best managed households. In hotels and restaurants, foods are generally prepared in great haste and are often only incompletely cooked. In such cases, it is not unreasonable to expect that some of the putrefactive and even pathogenic organisms originally present in sewage will still persist in the food and be taken by the consumers.

It is well known that digestive fluids—especially gastric juice—kill out most of the undesirable organisms present in food, but this may not always proceed satisfactorily. In some cases, the internal secretions may be inadequate or the organisms so numerous that some may escape destruction. The effect of this on the health of the consumer is still not properly understood. Systematic work on this aspect of the problem will yield results of considerable practical importance.

Taken on the whole, it would appear that sewaged crops—especially those of the market garden type—are not very desirable as articles of human food. On the other hand, farm animals flourish well on them. They are either immune or, at any rate, highly resistant to the effects of sewage pollution. It would appear to be highly desirable therefore to utilise sewage primarily for raising fodder or forage crops. The farm animals will, in turn, produce human food, which is comparatively safe to handle. In this manner the fertilising ingredients of sewage can be utilised to the maximum advantage and with safety to public health.

SUMMARY.

(1) The importance of sewage farming as an economical means of returning to the soil the various fertilising ingredients—especially nitrogen—originally removed from it in the form of crops is indicated.

(2) The nitrogen content of domestic sewage is determined by a number of factors, of which the nature of the wastes passing into the drainage and the water supply are the most important.

(3) The strength of sewage—especially in regard to nitrogenous constituents—varies with the season and, to some extent, with the time of day. The changes are not, however, very considerable when daily collections are mixed together prior to application to land.

(4) The difficulties arising through continued application of undiluted sewage—soil sickness, water pollution, plant diseases and insect pests—are indicated. Dilution of sewage with three to five times its volume of water—preferably after some system of pre-treatment involving the separation of sludge—eliminates the above-mentioned defects and leads to healthy crop production. Attention has also been drawn to the advantages of a modified system of treatment (involving addition of finely powdered cellulosic waste materials combined with intensive aeration) which yields a rich sludge containing practically all the nitrogen of sewage and an effluent which is quite innocuous.

(5) Even mere dilution followed by standing for some time lowers the albuminoid and the ammonia content of sewage. Nitrification—at any rate to the nitrite stage—proceeds quite rapidly. On application to land the oxidation is complete and, if the land is fallow, there is steady increase in the nitrate content of soil.

(6) When diluted sewage is applied to soil under crop, the nitrogen is taken up nearly as fast as it is applied. Addition of phosphatic or potassic fertilisers in small quantities has no direct effect on the transformations of nitrogen, but assist nitrogen intake by stimulating plant growth.

(7) Response of different crops to sewage irrigation has been discussed. Elephant grass raised on diluted effluent gave consistently higher yields than that irrigated with water. Lucerne did still better, the yield from sewaged plots being nearly three times that from the watered ones. Grain and market garden crops are also greatly favoured by diluted sewage. Basal dressing of phosphate is highly beneficial in some cases while, in others, very little improvement is observed.

(8) Fertilising value of sewage sludge—especially in regard to nitrogen—is indicated. Experiments with three different types of crops have shown that sewage sludge (activated sludge or the chemically precipitated product) is very much superior to mineral fertilisers (single or combined) applied on equivalent nitrogen basis.

(9) The physiology of crops raised on diluted sewage effluent has been

discussed. The beneficial effects are largely traceable to the steady supply of readily available nitrogen.

(10) Grasses and leaf crops in general respond best to sewage. They even tolerate undiluted sewage for fairly long periods. Among the market garden crops, some respond favourably, while others fail after some time.

(11) Sewaged crops do not keep so well as those irrigated with water. Some of the former also smell of sewage. It would be ordinarily difficult, however, to distinguish between the tastes of the two sets of products.

(12) Even under the most favourable conditions (including liberal dilution) sewaged crops cannot be entirely free from pollution. Careful washing combined with proper cooking will kill out most of the associated putrefactive and pathogenic organisms. When consumed, the digestive fluids will ordinarily destroy the rest. These operations may not, however, always proceed satisfactorily and, especially under certain unfavourable conditions, market garden crops raised on sewage may become a source of danger to public health. Farm animals, on the other hand, are fairly immune to pollution and do well on sewaged crops. In view of this and the fact that fodder and forage crops do best on sewage, it has been suggested that sewage farming may be mostly confined to raising such types of crops.

DECOMPOSITION OF OIL-CAKES AND FORMATION OF NITRATE.

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(Read at Symposium, August 29-30, 1936.)

Oil-cakes are valuable organic manures. They are in common use in Bengal for crops like potato, tobacco, sugar-cane, betel-vine, etc. They are applied in the *rabi* season for potato and tobacco and for sugar-cane and betel-vine in the *kharif.* The usual method of application is in the trenches or in the field at the time of the preparation of the soil and later on as a top dressing once or more according to the nature of the crop. In some places they are applied after preliminary rotting sets in by keeping the cakes mixed with earth in a pit and moistening the same with water.

It is a matter of common knowledge that oil-cakes take time to disintegrate and to become useful as plant food but nothing definite can be said on the point. The importance lies in the *time* of applying the cake to a quick growing crop ; if applied too early or too late there may be economic wastage, which is bad farming. In order to see how far the cultural practice followed in Bengal is suitable, i.e. how far the period of plant growth agrees or synchronises with the time of vigorous plant food formation (nitrate), and to find out the best time of application of the cake, an investigation was undertaken to study the decomposition of oil-cakes in the pot-culture house.

Eight tins each containing 30 lbs. of Dacca red soil have been taken. These tins have been coated inside and outside with a paint of tar. The scheme of the treatment is given below :—

(1) Soil only.
(2) Soil and lime.
(3) Soil and lime and castor cake (50 gms.).
(4) Soil and lime and groundnut cake (quantity of cake as in No. 3).
(5) Soil and lime and groundnut cake (mgms. N_2 as in No. 3).
(6) Soil and castor cake (quantity as in No. 3).
(7) Soil and groundnut cake (quantity as in No. 3).
(8) Soil and groundnut cake (quantity as in No. 5).

Soil taken   ..   30 lbs.

Lime applied   ∴   25 gms.
  (Nos. 2, 3, 4, and 5).

Castor cake   ..   50 gms. to supply 18·2 mgms. N_2 per 100 gms. dry soil.
  (Nos. 3 and 6).

Groundnut cake   ..   50 gms. to supply 32·6 mgms. N_2 per 100 gms. dry soil.
(Nos. 4 and 7).

Groundnut cake   ..   28·2 gms. to supply 18·2 mgms. N_2 per 100 gms. dry
(Nos. 5 and 8).   soil.

Percentage of nitrogen $\begin{cases} (a) \text{ Castor cake} \ldots \ldots 4\cdot40. \\ (b) \text{ Groundnut cake} \ldots 7\cdot80. \end{cases}$

All these tins have been kept inside the pot-culture house and the moisture content of the soil has been kept at about 18% by periodical addition of water. The soil in the tins has been sampled by an improvised auger from time to time and analysed for *nitrate* by the phenol-sulphonic acid method. The experiment continued from mid August to the 1st week of December.

TABLE 1.

Amount of nitrogen (mgms.) nitrate per 100 gms. dry soil.

Period of analysis	Treatment (1)	Treatment (2)	Treatment (3)	Treatment (4)	Treatment (5)	Treatment (6)	Treatment (7)	Treatment (8)
25th–28th August ..	5·55	5·09	3·65	3·84	5·65	5·25	3·37	3·94
1st–4th September ..	5·19	4·81	0·69	0·26	4·40	4·52	3·60	4·14
8th–11th September	4·90	5·20	0·69	*nil*	5·21	6·15	5·41	5·84
15th–18th September	4·39	5·86	0·90	*nil*	6·67	6·93	6·23	5·82
22nd–26th September	5·53	7·06	1·34	0·29	7·12	6·72	5·83	5·84
21st–24th October ..	5·45	7·95	4·96	9·73	8·89	6·62	8·00	6·87
3rd–6th November ..	4·51	7·48	8·53	19·39	7·90	6·05	6·60	6·91
10th–13th November	5·01	9·00	14·01	25·40	12·37	7·58	9·26	8·43
17th–20th November	6·30	11·42	17·45	29·65	15·22	8·60	12·68	9·85
24th–27th November	6·52	11·44	18·98	30·93	16·84	10·13	13·84	9·89
1st–4th December ..	6·44	11·61	18·99	31·18	17·49	9·90	13·81	9·91
Percentage of added nitrogen nitrated per 100 gms. dry soil (allowance being made for the nitrate in the soil with and without lime).		40·54	60·03	32·30	19·01	22·60	19·06

The analytical data are given in Table I and plotted in Graph 1. An examination of the figures shows that the addition of the cake causes at the start a slight depression in nitrification which lasts for a short time. The formation of nitrate, however, progresses gradually afterwards. The effect of preliminary depression and formation of nitrate afterwards is more pronounced when lime is added with the cake. The depression lasts for a longer time and is greater the larger the quantity of cake applied. During this period the nitrate concentration is reduced to a minimum. When the depression is over, a rapid rise in nitrification occurs. Lime intensifies nitrification. Thus, there is more accumulation of nitrate in the soil treated with lime than that in the untreated soil. With castor cake, the maximum percentage of added nitrogen nitrated during the course of the investigation has been roughly 19 as

against 40 with lime. Similarly, with groundnut cake (higher dose) the maximum percentage has been roughly 22 without lime and 60 with lime, and with the lower dose the corresponding figures are roughly 19 and 32 respectively. Of the two cakes, castor and groundnut, when equal amounts of nitrogen have been added nitrification is almost similar in both (about 19%) when applied without lime, but with lime castor cake does better than groundnut (40% as against 32%).

Regarding the depression in nitrification when cake is added to the soil it is first decomposed into nitrogenous and carbonaceous compounds. The latter in course of its further oxidation readily takes up oxygen from the air and the soil, while the nitrogenous compounds remain starved to a certain extent and nitrification makes headway only when the former reaction slows down. With lime, the decomposition of cake takes place more rapidly, resulting in the greater utilisation of available oxygen, and this probably explains the greater depression in nitrification at the early stage.

In order to follow the effect of nitrification on crops another series of experiments were started later on. The technique of the experiment has been the same as before, the only difference being that groundnut cake has been replaced by mustard cake and that two more similar series have been added. These two series have been sown with jute seeds and one of the series has been kept in the pot-culture house, while the other series has been kept outside. The tins in the latter series have been pierced with holes at the bottom to allow percolation and they have all been embedded in the field to approximate field conditions. The work began on the 25th May and lasted till the middle of September.

Nitrate formation has been studied periodically as before in all the three series of pots. The analytical figures are given in Table II.

Nitrification has followed a more or less parallel course as before. Here, too, lime has depressed nitrification at the start and later on has intensified it. It may be noted that in a few cases abnormal nitrification has been observed. This may be attributed to defective mixing of the cake with the soil and to error in sampling.

The next point of interest is the effect of cake on the jute crop. On comparing the two series of pots, one inside and the other outside the pot culture house, it has been observed that the plants in the inside pots died before they were barely 2″ to 3″ high, except in 3 pots, where they had a precarious existence, the maximum height being about 4″, while the plants in the outside pots had a normal growth. On examination of the nitrate figures it is seen that the concentration of nitrate had been very high in the inside pots. About the middle of July, when the inside plants were only 2″ and were decaying, the outside plants were healthy and making normal growth. The concentration of nitrate was of the order 10-15 in the inside pots as against 2 to 6 outside. The failure of plants inside may be attributed to the high concentration of nitrate, which the plants could not stand, while outside the

TABLE II.

Nitrogen nitrated per 100 gms. of dry soil (in milligrams)

Date of analysis

		May 27	June 5	June 22	June 30	July 8	July 23	August 5	Sept. 2	Sept. 15
1. Treatment (1)	..	4·88	6·90	8·84	8·38	9·67	10·85	11·41	13·40	11·67
2. Do. (2)	..	2·85	6·68	7·00	7·55	7·89	10·72	13·06	21·57	11·57
3. Do. (3)	..	5·82	7·37	7·25	7·97	8·41	9·19	16·61	18·40	14·62
4. Do. (4)	..	2·38	5·14	15·89	21·48	19·02	31·78	34·96	36·88	27·30
5. Do. (5)	..	6·18	10·01	7·41	6·85	9·92	10·28	13·14	17·19	18·36
6. Do. (6)	..	2·86	5·16	12·73	14·43	15·24	18·34	34·78	56·81	31·70
7. Do. (7)	..	3·71	9·60	7·95	9·41	12·54	16·19	18·90	46·38	37·93
8. Do. (8)	..	2·36	5·06	12·03	15·66	18·34	29·35	23·25	26·35	30·34
9. Same as (1)	Kept inside the pot-culture house.	5·27	4·79	4·11	5·48	6·59	8·59	7·39	8·00	....
10. Do. (2)		4·74	5·70	7·72	8·02	10·43	10·73	10·82	10·34	....
11. Do. (3)		8·38	4·79	8·06	11·74	9·30	14·86	17·08	13·23	....
12. Do. (4)		3·63	4·33	15·02	23·98	25·74	31·24	35·64	29·10	....
13. Do. (5)		7·51	6·06	7·28	9·44	7·32	13·14	23·26	12·35	....
14. Do. (6)		2·55	3·65	10·98	12·37	15·27	18·16	16·44	17·42	....
15. Do. (7)		14·32	7·67	7·51	11·06	9·31	12·05	14·63	27·02	....
16. Do. (8)		2·31	3·04	14·59	20·87	16·62	23·63	18·23	19·04	....
17. Do. (1)	Kept in the field.	4·32	3·81	0·95	1·37	1·99	1·05	0·62	nil	nil
18. Do. (2)		5·33	4·70	0·97	0·86	0·79	nil	0·35	nil	nil
19. Do. (3)		6·18	6·29	5·57	....	5·95	5·15	6·92	1·07	nil
20. Do. (4)		3·92	3·61	4·83	5·22	6·43	0·79	nil	nil	nil
21. Do. (5)		6·81	8·26	2·45	0·86	6·00	3·19	4·37	nil	nil
22. Do. (6)		4·34	4·87	4·59	3·72	5·40	3·35	1·09	nil	nil
23. Do. (7)		10·79	7·90	....	3·52	7·77	5·18	4·60	3·17	nil
24. Do. (8)		4·14	3·14	....	3·45	4·69	0·96	nil	nil	nil
Rainfall between successive analysis in inches.	..	..	3·87	7·03	1·22	7·37	1·32	7·94	3·03

Note.—Treatment (1), (9), and (17)—Soil only (30 lbs.).

Treatment (2), (10), and (18)—Soil (30 lbs.)+Lime (25 gms.).

Treatment (3), (11), and (19)—Soil (30 lbs.)+Castor Cake (55 gms.) equivalent to 30 mgms. N_2 per 100 gms. dry soil.

Treatment (4), (12), and (20)—Soil (30 lbs.)+Castor Cake (55 gms.) equivalent to 30 mgms. N_2 per 100 gms. dry soil+Lime (25 gms.).

Treatment (5), (13), and (21)—Soil (30 lbs.)+Mustard Cake 55 gms. (20 mgms. N_2).

Treatment (6), (14), and (22)—Soil (30 lbs.)+Lime (25 gms.)+Mustard Cake (small dose) 55 gms. (20 mgms. N_2).

Treatment (7), (15), and (23)—Soil (30 lbs.)+Mustard Cake (big dose) 82 gms. (30 mgms. N_2).

Treatment (8), (16), and (24)—Soil (30 lbs.)+Lime (25 gms.)+Mustard Cake (big dose) 82 gms. (30 mgms. N_2).

Remarks.—Pots 9 to 16 have been sown with jute and kept inside the pot-culture house.

Pots 17 to 24 have been similarly sown with jute but kept outside the pot-culture house and embedded in the field.

nitrate formed was mostly washed off by the rains and the residual nitrates were sufficient for the growth of the plants. It may be noted that the limed pots recorded higher yields than the unlimed ones. Another point to be noted is that with cake nitrification commences vigorously 6 to 8 weeks after its application and the nitrate goes on accumulating until the heavy rains of the monsoon wash off most of the nitrate. This is an economical loss of great significance. From a practical standpoint the application of cake should be so made as to enable the crop to utilise the nitrate as much as possible before it is washed off. This points to the advisability of the application of cake during the *rabi* season so that the *kharif* crop, following a *rabi* crop, may derive the maximum benefit of the nitrate which remains unutilised by the *rabi* crop, and which is formed afresh by the further decomposition of the cake. In no case should the cake be applied in the *kharif* season for quick growing crops, as in that case there is the great risk of loss of a considerable portion of the nitrate made available by the further decomposition of the cake.

The present practice of applying cake in the *rabi* season for potato seems to be a sound one as the succeeding crop, usually jute, can fully utilise the unspent and freshly formed nitrate. As mentioned before cake is applied in the *kharif* season for crops like sugar-cane and betel-vine. Of these, betel-vine is a perennial crop while sugar-cane is almost a full year crop. The application of cake in the *kharif* season no doubt involves a great risk of loss of nitrate, but the well-established root systems enable sugar-cane and betel-vine to utilise the nitrate as soon as it is formed. So the loss of nitrate by washing during the rains is minimised to a great extent.

SUMMARY

The decomposition of 3 kinds of oil-cakes in soil with and without lime and the formation of nitrate therefrom has been studied.

After a preliminary depression lasting for a short time nitrification goes on vigorously. Addition of lime quickens the decomposition of the cake and intensifies the nitrification.

The influence of nitrate on jute has been studied in pots. High concentration of nitrate in soil has been found to inhibit the growth and ultimately to result in the total failure of jute.

The heavy rains during the monsoon wash off most of the nitrates from the soil and hence the application of cake in the *kharif* season precludes the possibility of deriving maximum benefit. The present practice of the application of cake as a manure has been discussed. The application of cake during the *rabi* season appears to be more sound.

TRANSFORMATIONS OF NITROGEN IN THE SWAMP SOIL.

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(Read at Symposium, August 29-30, 1936.)

Mineralisation of the organic soil nitrogen is essentially a biological process, consisting of two well defined stages—ammonification and nitrification. The quantity of mineralised nitrogen may be inferred from the amounts of ammonia and nitrates that are formed. In dry soils, ammonification proceeds much slower than nitrification, so that the greater part of the mineralised nitrogen is found in the form of nitrates. The rate of nitrification will thus serve as a means of measuring the comparative rate of organic nitrogen transformation. Such, however, is not the case with the swamp soil. A number of investigators have shown that under such conditions nitrates are not formed and, even if present, are quickly converted into nitrites and are finally lost or denitrified (Warington, 1892, 1897 ; Nagaoka, 1903, 1904, 1906 ; Daikuhara and Imasaki, 1907 ; Kelley, 1911 ; Oelsner, 1918 ; Janssen and Metzger, 1928 ; Bartholomew, 1929 ; Joachim and Kandiah, 1929 ; Mukerji and Vishnoi, 1936 ; and others). According to Harrison and Iyer (1912–16), bulky organic manures yield ammonia under the conditions of the rice soil, there being no nitrification, although the major part of the nitrogen is lost in the elementary state. Subrahmanyan (1927, 1929) observed that in the absence of freshly decomposing organic materials, water-logging results in slight diminution in nitric nitrogen and a distinct increase in free and saline ammonia ; the formation of ammonia has been shown to be enzymic in origin. In presence of fermenting organic matter, even added nitrates are completely lost.

It is not clear whether all the nitrogen thus rendered available in the form of ammonia is utilised by the plant. The amount of available nitrogen in the soil is a balance between the nitrogen liberated from the decomposition of the organic matter and that absorbed by the micro-organisms which decompose the non-nitrogenous and nitrogenous constituents. In dry cultivated soils there have been a number of studies relating to the importance of the composition of organic materials in determining the availability of their nitrogen in the soil (Thomas and Harper, 1926 ; Blair and Prince, 1928 ; Waksman, 1926 ; Waksman and Tenney, 1928 ; Jensen, 1929 ; Martin, 1930 ; Lemmermann, Jensen and Engel, 1930 ; Sievers, 1930 ; Smith and Humfeld, 1930 ; Salter, 1931 ; and others.) The supply of easily available nitrogen is also known to be an important factor in determining the rate of organic matter decomposition

TABLE I.

Changes in ammonia production and in total nitrogen.

Nitrogen as parts per million

Material used	C-N ratio of material	Days											
		0		8		29		57		78		170	
		NH$_3$-N	Total N	NH$_3$-N	Total N	NH$_3$-N	Total N	NH$_3$-N	Total N	NH$_3$-N	Total N	NH$_3$-N	Total N
Dried blood	3·3	..	530	48·0	500	79·8	440	100·7	400	100·0	360	66·9	320
Urea	0·4	..	530	95·1	520	186·9	400	126·2	330	121·5	300	42·2	280
Hongay leaf	13·8	..	530	20·0	520	54·1	480	66·8	450	67·3	420	43·6	390
Farmyard manure	9·8	..	530	4·6	530	10·2	520	7·0	490	2·8	460	1·9	380
Lantana	22·6	..	530	2·3	530	2·8	530	1·9	520	0·5	520	0·9	460
Straw	120·3	..	530	..	..	0·5	530	0·9	530	..	520	..	500
Untreated soil (control)	(10·0)	1·2	230	1·2	230	2·3	230	..	..	..	220	1·4	210

(Meakle, 1918 ; Starkey, 1924 ; Waksman and Starkey, 1924 ; Barthel and Bengtsson, 1924 ; Anderson, 1926 ; Waksman, 1927 ; and others). The position in regard to the swamp soil is not, however, so well defined although a few workers (Itano and Arakawa, 1927 ; Osugi, Yoshie and Komatsubara, 1931) have studied the decomposition of organic materials under such conditions.

The present investigation relates to the transformations in the swamp soil of organic nitrogen from widely different sources, the nature of the losses of nitrogen taking place under such conditions and the means whereby it can be either prevented or, at any rate, reduced to a minimum.

EXPERIMENTAL.

The soil (100 g. lots) was treated with different organic materials in quantities corresponding to 30 mg. of nitrogen. The substances employed were urea, dried blood, hongay leaf, farmyard manure, lantana and rice straw respectively. The mixtures were then swamped and allowed to decompose at 30° and the changes in the different forms of nitrogen (ammoniacal, nitrate, and total) followed in samples taken from time to time.

It was observed that, in general, ammonification proceeded faster with substances with narrow C-N ratios than with the others. With substances of very wide C-N ratios, there was practically no ammonification. The quantities of ammonia formed in the medium tended to increase during the first 8 to 10 weeks after which there was a steady decrease. Nitrification was observed only in the case of substances with narrow C-N ratios and the production of nitrate generally commenced only after about a month when the vigour of the initial fermentation had subsided and fairly large quantities of ammonia had accumulated in the system. There was progressive loss of nitrogen in almost all the cases and, as may be seen from Table I, although the production of ammonia or the loss of nitrogen varied widely for the different substances, there was a close relationship between the two. Thus, substances like dried blood and urea, which ammonify rapidly, also lose their nitrogen at a fast rate, while substances like hongay leaf which ammonify at a somewhat moderate rate do not lose their nitrogen so rapidly. On the other hand, there is very little loss of nitrogen with substances like lantana and straw which also exhibit very little ammonification.

Addition of increasing quantities of fermenting organic matter (10, 20, 30 and 40 mg. respectively of nitrogen added as dried blood to 100 g. lots of soil) resulted in corresponding increase in the production of ammonia and in greater losses of nitrogen (Table II).

The results of experiments carried out with mixtures of organic materials in such proportions as would give a C-N ratio of about 15 to 1 and in quantities corresponding to 30 mg. of nitrogen per 100 g. of soil (Table III) would, however, show that the extent of mineralisation and the loss of nitrogen can be adequately controlled by adjusting the ratio of carbon to nitrogen.

TABLE II.

Changes in total and ammonia nitrogen in presence of increasing quantities of dried blood.

Mg. nitrogen added as dried blood	DAYS.									
	0		8		29		57		78	
	NH_3-N	Total N	NH_3-N	Total N	NH_3-N	Total N	NH_3-N	Total N	NH_3-N	Total N
	Nitrogen in parts per million									
10	..	330	16	310	28	290	19	290	7	280
20	..	430	23	400	73	390	58	370	33	350
30	..	530	48	500	80	440	101	400	100	360
40	..	630	43	590	132	500	130	440	..	400

TABLE III.

Changes in ammonia and in total nitrogen in presence of mixtures of materials adjusted to C-N ratio, 15 : 1.

Materials mixed	DAYS									
	0		8		29		57		78	
	NH_3-N	Total N	NH_3-N	Total N	NH_3-N	Total N	NH_3-N	Total N	NH_3-N	Total N
	Nitrogen expressed as parts per million									
Lantana + Dried blood ..	..	530	1·2	490	6·2	480	16	480	28	480
Urea + Glucose	..	530	10·4	470	163	470	144	440	160	420
Urea alone .. (control)	..	530	95·1	520	187	400	126	330	122	300

From Table III can be seen that the production of ammonia from urea was not appreciably checked by the presence of glucose ; in a like manner dried blood also would seem to ammonify independently of the presence of lantana. The amounts of ammonia were, however, small in this case because of the small quantity (less than 0·1 gm.) of dried blood itself present in the medium. On the other hand, it may be noted that the loss of nitrogen from urea or from dried blood (*cf.* Table I) has been greatly retarded by the presence of their respective components. The mechanism of the retention of nitrogen is still obscure. The steady increase in the ammonia content of the medium would suggest that ammonification was not retarded by the presence

of the added components.   The non-volatilisation of the ammonia thus formed
would, on the other hand, point to its being in some combined form, probably
as a salt.

Attention has already been drawn to the fact that pure carbohydrates,
as also substances with wide C-N ratios, undergo fermentation in the soil
yielding organic acids.   If we assume that the ammonification of the added
nitrogenous material and the acid fermentation of the carbohydrate or
cellulosic material proceeded side by side, then the ammonia resulting from
the former would combine with the acids produced by the latter.   In this
manner, volatilisation of ammonia and consequent loss of nitrogen would be
largely prevented.

The observations that nitrogen loss was greatest with substances which
underwent the most rapid ammonification suggested that a part at least of
the loss might have been due to volatilisation as ammonia.   Experiments
conducted with soil treated with urea and dried blood respectively (50 mg.
N for 100 g. of soil) indeed showed that ammonia was the chief nitrogenous
product among the gases evolved and accounted for the major part of the

TABLE IV.

Loss of nitrogen and volatilisation of ammonia.

Treatment		DAYS					
		8	15	22	29	57	78
UREA (Swamped) ..	Loss of total nitrogen (mgs.)	0·6	2·8	4·8	16·2	19·2	..
	Loss as ammonia (mgs.)	0·5	2·3	4·6	..	15·8	19·0
DRIED BLOOD (Swamped) ..	Loss of total nitrogen (mgs.)	1·6	5·3	10·4	14·1	20·7	24·1
	Loss as ammonia (mgs.)	1·6	4·1	8·8	12·3	17·6	20·8
DRIED BLOOD (maintained at 60% satura- tion).	Loss of total nitrogen (mgs.)	0·6	3·0	4·1	5·3	7·1	10·4
	Loss as ammonia (mgs.)	0·2	1·4	2·3	3·2	4·3	6·2

Nitrogen originally added = 50 mg.

nitrogen lost from the soil system (Table IV).   Similar experiments carried out
with soil treated with dried blood but maintained at 60 per cent saturation
also showed that the major part of the loss was by volatilisation as ammonia.

DISCUSSION.

Under the conditions of the swamp soil ammonification proceeds at a much
faster rate than nitrification.   There would therefore be an accumulation of

ammonia in the soil system and consequent loss by volatilisation. However, as may be seen from the above studies, there is very little loss of nitrogen during the early stages of fermentation when the dissolved oxygen content of the medium is low and when the soil reaction is fairly acid and contains useful amounts of free organic acids (chiefly lactic and acetic). It is only after the first few weeks, when more or less aerobic conditions are restored and nitrification sets in, that the loss of nitrogen from the soil system is most pronounced. Although it has been suggested that the losses of nitrogen occurring under the ' anaerobic ' conditions of the swamp soil may be due to denitrification, the results of the present enquiry would suggest that volatilisation of ammonia proceeds under conditions which are the very reverse of those favouring denitrification.

The nitrogen losses observed in the present studies are rather considerable, but these will be much less in the presence of the growing plant. Still, among the conditions which determine the rapidity of decomposition of organic materials added to the soil temperature is of the greatest importance, and in tropical regions the temperature prevailing in the rice soils is bound to be high and the decomposition may proceed at a fast rate. The organic matter resulting from such decomposition will have a narrower C-N ratio and the losses of nitrogen may thus be enormous, due both to the greater decomposition and to the fact that less of organic matter will be synthesised by the micro-organisms concerned. Such losses may, as would appear from this study, be profitably reduced by adding the substances in small lots at a time or in presence of immobilisers which would retain the surplus nitrogen in combined forms.

SUMMARY.

Decomposition of organic materials (such as urea, dried blood, farmyard manure, green manure and seed cake) in the swamp soil results in the production of ammonia. The extent of such production is determined by the C-N ratio of the materials applied, being more with substances of narrow ratios than with those of wide ones.

Addition of increasing quantities of organic materials results in proportionately greater production of ammonia followed by correspondingly heavier loss of nitrogen. The loss is most pronounced in the case of substances with narrow C-N ratios.

An enquiry into the mechanism of the loss of nitrogen has shown that this occurs largely through volatilisation of ammonia from the soil system. It has been found that, under the swamp soil conditions, ammonification proceeds much faster than nitrification, so that there is accumulation of ammonia in the medium. The volatilisation of ammonia is favoured by the high temperature prevalent under tropical conditions.

Addition of carbonaceous materials calculated to widen the C-N ratio to 15 : 1 or more is effective in reducing the loss of nitrogen.

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SOME FIELD AND WATER CULTURE EXPERIMENTS WITH RICE.

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(Read at Symposium, August 29-30, 1936.)

The results of these experiments have a direct bearing on the available nitrogen status of the soil and as such is reported here.

1. Assimilation of Nitrogen by the Rice Plant.

The estimation of the weight and the percentage of nitrogen in the dry matter of 15 rice plants collected at random from an unmanured paddy field at eight different stages of growth from transplantation to harvest shows the following facts :—

TABLE 1.

	Before ear emergence.					After ear emergence.		
Sample ..	1	2	3	4	5	6	7	8
Weeks after transplantation ..	0	3	6	9	12	14	16	18
Weight of dry matter in gms. ..	4·38	7·7	20·7	95·8	194·6	330·9	540·3	538·2
Percentage of N (whole plant) ..	1·255	1·87	2·34	2·22	1·545	1·132	0·867	0·698
Total N in gms. ..	0·054	0·143	0·485	2·127	3·008	3·745	4·69	3·76
Wt. of N as % of the maximum	1·1	3·1	10·3	45·7	64·0	79·8	100	80·2
Absorption of N per week in gms. ..	·03	·114	·547	·294	·369	·473	−·47	..

The percentage of nitrogen in the rice plant increased until about six weeks after transplantation and thereafter decreased steadily until harvest. Since the weight of the dry matter increased from transplantation onwards, there can be only one reason for the rise in the percentage of nitrogen, viz. nitrogen was assimilated at a faster rate in comparison with carbon. Similarly the subsequent fall in the percentage of nitrogen was due to the assimilation of nitrogen at a slower rate than that of carbon. The determination of available nitrogen in the soil showed that the little nitrate that was present disappeared when the soil was water-logged, but ammonia accumulated until about six weeks from transplantation, when it fell off rapidly. Obviously

during the first six weeks after transplantation more ammonia was produced in the soil than the plant could consume. And as a result of this abundance of ammonia nitrogen was assimilated at a faster rate than carbon leading to the increase of percentage of nitrogen in the plant. On the other hand the period immediately following the sixth week after transplantation corresponded with the vigorous stage of plant growth. The demand for ammonia at this stage by the plant was greater in proportion to its production in the soil. In consequence soil ammonia decreased rapidly, which in turn resulted in the assimilation of ammonia nitrogen at a slower rate than carbon, leading to the fall in the percentage of nitrogen in the plant. It is therefore clear that available nitrogen status of the soil markedly affects the nitrogen composition of the crop especially during the early stages.

Furthermore, of the maximum quantity of nitrogen eventually absorbed by the rice plant two-thirds was only taken up at flowering (sixth row in the above table). During the milk stage therefore a considerable amount of nitrogen was assimilated. If the rate of absorption per week is considered (last row in the table), it will be found to shoot up again during this period. From the point of view of practical agriculture, therefore, it may pay to increase the available nitrogen status of the soil by manuring at this stage also.

A loss of nitrogen from the rice plant is indicated during the ripening stage but this requires further confirmation.

2. NITROGEN REQUIREMENT OF THE RICE PLANT.

In the preceding experiment the importance of maintaining an available nitrogen status in the soil almost throughout the life of the rice plant has been stressed. But it will be interesting to see what happens to the plant if the supply of nitrogen falls short or becomes nil after the plant has grown for sometime. Accordingly rice plants were grown in culture solutions containing all essential elements, N, K, P, Ca, Mg, S, and Fe up to different stages of growth and then transferred to solutions containing these elements excepting nitrogen. It was found that the growth of the plant was checked in absence of nitrogen at any stage, but the plant, even the four-week old seedling, managed to survive and eventually bore grain. In all cases nitrogen was found to increase in the plant during the period it lived in culture solutions without nitrogen. This indicated the possible capacity of the plant to assimilate elemental nitrogen. Similar observation was made in a sand culture experiment with rice and has been reported in a separate paper on the ' Nitrogen Supply of Rice ' for the Symposium.

On the other hand it will also be interesting to see what happens to the plant if the available nitrogen status in the soil becomes excessive, say by over manuring, or otherwise. It was found that when the rice plant in water culture was fed with increasing doses of nitrogen, the percentage of nitrogen in the straw and the seed increased, the total number of the filled seeds per ear

decreased, the total number of the empty seeds increased in proportion to the filled seeds, until the dose became such that all the seeds which appeared were empty and finally, when the percentage of nitrogen in the straw at harvest was 1·25 due to excessive nitrogen, no seed formation took place at all.

The adverse effect of excessive nitrogen on seed production was counteracted to some extent by the presence of boron in the culture solution. Boron stimulated both vegetative growth and seed formation. It was further found that the rice plant absorbed as much nitrogen in presence of boron as it did in its absence, but the total dry matter at harvest in the former case was almost double that in the other case. It is suggested that the beneficial influence of boron on seed formation lies not as much in controlling the absorption of nitrogen as in correcting the physiology of the plant by stimulating a proportionate increase in the carbon assimilation by the latter. Further experiments showed that this beneficial effect of boron was independent of its concentration from 1 p.p.m. to 12 p.p.m. in the culture solution. Higher concentrations were not tried as they might prove toxic.

3. LOSS OF NITROGEN FROM CULTURE SOLUTIONS.

That loss of nitrogen takes place in submerged paddy fields as elemental nitrogen has been shown by several previous workers. In the water culture experiments reported here it was observed that there was considerable loss of nitrogen from culture solutions under rice. When there was no crop there was little or no loss from culture solutions. Of the total loss under rice roughly about 50% was recovered in the plant. The remaining 50% was lost probably as elemental nitrogen. This was true whether nitrate or ammonia was present in the culture solutions. Further experiments were carried out to determine the extent of this loss at various stages of the plant growth. The results were as follows :—

During	Loss of nitrogen, probably as elemental nitrogen, as per cent of total loss from culture solution.
Seedling Stage	46.1
Active Vegetative Stage	6.4
Flowering Stage	21.5
Ripening Stage	60.9

It is clear that the loss of nitrogen from the culture solutions is very great during the seedling and ripening stages. The result is of obvious importance as it demonstrates the advisability of increasing the available nitrogen status of the soil, if so desired, by top dressing of soluble nitrogenous fertilisers only during the active vegetative stage and in the beginning of the flowering stage.

4. MANURING OF A LATERITIC PADDY FIELD WITH NICIPHOS.

For this experiment 72 plots were laid out in three blocks of 24 plots each in the Government Farm, Dacca. The soil is of a lateritic type and poor in organic matter and nitrogen status. Twelve treatments consisting of various combinations of lime, potash, and magnesium were distributed in 36 plots. The remaining 36 plots received the same 12 treatments plus niciphos at the rate of 130 lbs. per acre given in two doses as top dressings—one at the end of the seedling stage and the other during the middle of the active vegetative stage. Experiments have now been carried out for about 5 years in these two sets of 36 plots receiving no nitrogen and niciphos respectively. The results show that the increase in the grain yield due to niciphos is statistically significant but the increase even in a year of favourable weather conditions averages to only 21 per cent over the yield of the plots receiving no nitrogen.

MANURIAL TREATMENT FOR REMEDYING NITROGEN DEFICIENCY OF SOILS OF UPPER ASSAM FOR GROWING PLANT CANES.

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(Read at Symposium, August 29-30, 1936.)

This paper deals with the results of some of the sugar-cane experiments that have been done at Jorhat Farm, and as the soil of the Farm is more or less representative of some of the soils of the Upper Assam Valley, some idea can be formed from these experiments as to the status of nitrogen in such soils. The nitrogen content in Jorhat Farm soil is on an average ·09% (top-soil) and sugar-cane, when grown without any nitrogenous manurial treatment, has been found to give very poor yield of canes ; stunted growth and other signs of nitrogen starvation were invariably noticed. It has been the usual practice in the Farm to manure the canes of the nursery and simple varietal experimental plots with 300 mds. of cow-dung+1,000 lbs. of oil-cake in the case of plant canes and with 200 mds. of cow-dung+2,000 lbs. oil-cake in the case of ratoon canes. Besides, in simple varietal and manurial experiments the following rotation is followed :—

1st year—plant cane.
2nd year—ratoon cane.
3rd year—(Kharif) a green manure crop, (rabi) oats.
4th year—(Kharif) another green manure crop, (rabi) a catch crop of mustard.

Canes under the above arrangements are found to yield a good crop, the maximum yield up to 1936 being 54 tons approximately per acre of stripped canes with Co. 419 (Plant cane).

A good idea as to yields of canes when grown under different treatments, viz. (1) control, (2) $\dfrac{125 \text{ mds.}}{50 \text{ lbs. N}_2}$ cow-dung per acre, (3) $\dfrac{250 \text{ mds.}}{100 \text{ lbs. N}_2}$ cow-dung per acre, can be gathered from the combined varietal and manurial experiment conducted in the year 1935-36. The above mentioned treatments were used with three varieties of plant canes, P.O.J. 2714, Co. 213, Teli, and the experiment was laid out in the randomised blocks with 3 replications. The soil of the experiment received no initial common manurial dressing. Signs of nitrogen starvation was noticed in the case of treatment (1), to some extent in treatment (2), and to a very small extent in the case of treatment (3). In the latter case both the yield of stripped canes and quality of juice were found to be superior to those due to other treatments, the yield of canes under treatment (1) being extremely poor. The experiment clearly showed that

nitrogen is not present in the soil in a form to yield a satisfactory crop. It must be added to the soil in the form of a suitable manure.

The results, given below, of our manurial experiment conducted in the year 1934-35 clearly show the utility of using 300 mds. cow-dung+1,000 lbs. oil-cake—the usual treatment given to plant canes in the nursery and simple varietal experiments in our Farm.

Manurial Experiment, 1934-35.

With Co. 213 (Plant canes), 4 treatments with six replications.

Treatment (1)—100 mds. cow-dung.
,, (2)—200 ,, ,,
,, (3)—300 ,, ,,
,, (4)—400 ,, ,,

Treatment	1	2	3	4	Mean	S.E.
Yield of stripped canes (ton per acre)	23·13	24·92	27·44	26·83	25·60	·699
Sucrose tons per acre ..	2·16	2·28	2·40	2·33	2·29	·103
% Sucrose in juice ..	14·69	14·85	14·16	14·19	14·47	·29
% Glucose in juice ..	·52	·69	·71	·58	·63	·046

All plots received a common dressing of 1,000 lbs. oil-cake.

Conclusions :—For stripped canes treatment 3 is the best and significantly greater than treatment 1 or 2.

Regarding sucrose content treatment 3 yields the highest value but is not significantly greater than the others.

Further experiments are in progress. These include tests in fields of cultivators in selected areas. Each of the treatments stated above indicates the amount per acre.

SOME FACTORS INFLUENCING STUDIES ON NITROGEN FLUCTUATIONS IN SOIL PLOTS.

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Fluctuations in the total nitrogen, ammonia, and nitrate contents of arable land have been reported by a number of workers (Leather, 1911 ; Russell, 1914 ; Russell and Appleyard, 1917 ; Waynick, 1918 ; Waynick and Sharp, 1918 ; Lemmermann and Wichers, 1920 ; Thornton and associates, 1927, 1930 ; Clarke, 1922 ; Annett *et al.*, 1928 ; Smith, 1928; Prescott and Piper, 1930 ; Batham and Nigam, 1930 ; Penman and Rountree, 1932; Bartholomew, 1932 ; Sreenivasan and Subrahmanyan, 1934 ; Wilshaw, 1934 and others). A few workers (Prescott and Piper, 1914, 1930 ; Annett *et al., loc. cit.* ; Batham and Nigam, *loc. cit.* ; Sahasrabuddhe and Co-workers, 1927, 1931, 1932, 1936 ; Wilshaw, *loc. cit.* and others) have noted that such variations depend on season, temperature, rainfall, moisture content of soil and other factors. Definite recuperation of nitrogen in the soils has also been shown to proceed under favourable conditions of moisture, temperature, aeration, and manuring (Wilsdon and Ali, 1922 ; Annett *et al., loc. cit.* ; Sahasrabuddhe and Co-workers, *loc. cit.* ; Desai, 1933 ; Garlach, 1934 ; Vandecaveye and Villanueva, 1934, Wilshaw, *loc. cit.* ; and others).

The magnitude of experimental error attaching to investigations of this kind is a function of two probable errors, namely, (1) the laboratory error, i.e. the error of analytical determination, and (2) the field error, which is the error due to the normal variation in the composition of the soil from point to point in the field. The former may also include the error of sampling from the laboratory sample. In the present communication it is proposed to examine the significance of these two factors in regard to the nature and extent of the changes in soil nitrogen.

THE ERROR IN ANALYTICAL METHODS OF NITROGEN DETERMINATION.

Total nitrogen in soils is usually determined by the Kjeldhal method. The application of this method to soils has generally been considered to be reliable until Bal (1925) showed that certain types of soils—such as those of the black cotton areas of the Central Provinces in India—offer considerable resistance to acid digestion and yield invariably low and inconsistent estimates of total nitrogen. He showed that this was due to inadequate penetration of the soil by concentrated sulphuric acid and recommended pre-treatment with water to overcome this difficulty. Higher and more consistent estimates

of nitrogen were thus obtained.   The significance of this important observation was not first realised, due probably to the impression that it related only to a particular type of soil.   The later observations of Sreenivasan (1932) showed, however, that it applied to other types of soils as well.   'Dry' digestion generally yielded low estimates of nitrogen, whereas pre-treatment with water or, preferably, dilute acid led to smoother digestion and to higher and more consistent values being obtained.   Thus, in Table I are recorded the values for total nitrogen obtained by the 'Dry' and 'Wet' methods for a number of Indian soils (Sreenivasan and Subrahmanyan, 1933).

TABLE I

Nitrogen contents of some tropical soils as determined by 'Wet' and 'Dry' methods.

Soil from	Description	Nitrogen as p.p.m. (averages)		Difference ('Wet'-'Dry') per cent. 'Wet' = 100
		'Dry'	'Wet'	
Kottayam	Red gravel-surface	978	972	— (0·7)
Cuttack	Low land-surface	754	768	+1·8
Kandy-Ceylon	Laterite-tea soil	1,437	1,471	+2·3
Jaffna-Ceylon	Sandy-surface	313	322	+2·8
Dacca	High land-surface	820	843	+2·8
Kottayam	Sandy-wet cultivation	433	442	+2·0
Travancore	Sandyloam-surface	140	144	+3·1
Tellicherry	Red Sandyloam-surface	679	692	+1·9
Bangalore	Lateritic-surface	211	220	+4·1
Do.	Red loam-surface	536	566	+5·3
Punjab	Rice land-surface	944	988	+4·5
Nasik	Dry land-surface	856	908	+5·7
Bangalore	Light-surface	901	934	+3·5
S. Bihar	Alluvial-surface	440	470	+6·6
N. Bihar	Calcareous	389	419	+7·4
Tindivanam	Loam-alkaline-surface	175	191	+8·2
Tellicherry	Heavy clay-surface	967	1,049	+7·8
Sholapur	Light clay-surface	297	339	+12·4
Mandalay	Rice land-surface	472	544	+13·2
Nandyal	Red clay-subsoil	273	313	+12·8
Do.	Do. surface	248	304	+18·3
Nagpur	Heavy black-surface	648	746	+13·1
Sholapur	Medium black-subsoil	326	395	+17·5
Do.	Heavy black-subsoil	310	411	+24·4
Indore	Black cotton-surface	395	533	+25·9

While invariably low and discordant values for nitrogen are obtained by the official 'dry' method, the inaccuracy of the estimate obtained as above is sometimes as high as 26 per cent.

The advantages of pre-treatment with water are being recognised by other workers as well (Martin and Griffith, 1935 ; Walkley, 1935 ; Ashton, 1936). Walkley (1935) has also recorded instances of certain English (heavy alkaline) soils which give highly inaccurate results by the usual 'dry' method.

Similar errors are introduced in following the course of nitrogen transformations in the soil as may be seen from the following experimental results. Soil (100 g. lots) was treated with dried blood (corresponding to 50 mg. N). In one set of experiments, the specimens were moistened with water and maintained at 60 per cent saturation, while the others were treated with enough water to maintain the mixtures in a water-logged condition. At stated intervals, samples were removed and the total nitrogen determined both by the official 'dry' method and after pre-treatment with water (Table II).

TABLE II

Transformations of nitrogen in soils.

Treatment	Method of diges- tion	Total nitrogen in parts per million (averages).							Stan- dard error
		Time of days							
		0	8	15	22	29	57	78	
Maintained at 60 per cent saturation	'Dry'	711	689	669	655	645	617	595	±0·2
	'Wet'	730	724	700	689	677	659	626	Small
Water-logged	'Dry'	711	675	636	580	541	464	422	±1·2
	'Wet'	730	714	677	626	589	523	489	Small

The difference between the values obtained by the two methods becomes increasingly prominent with time. This is strikingly so in the case of the water-logged specimens in which the loss of nitrogen on the 78th day is apparently 16 per cent more according to the 'dry' method than by the 'wet' one. The results thus show that the present official methods are not reliable for the accurate study of nitrogen transformations in soils.

It has been observed by the present authors that even in finely ground and apparently homogeneous specimens of soils, such as are used for analytical work in the laboratory, the distribution of nitrogen is not uniform, so that it is not possible to obtain concordant estimates unless the entire specimen is mixed up repeatedly and carefully resampled from time to time. It is therefore to be recognised that the variability of the total nitrogen content of soils will not be great unless the method of determining total nitrogen is accurate and reliable. The present official 'dry' method is not sufficiently accurate to cause appreciable variability among a huge number of samples taken from a small area, and, as emphasised by Bal (1927), 'the important factor of the method of nitrogen determination has to be taken into consideration while formulating any conclusions regarding the work on nitrogen fixation in soils in general and heavy soils in particular'.

THE ERROR IN FIELD SAMPLING.

The total nitrogen contents of different plots (11′×11′)—apparently uniform—and manured with farmyard manure at 22 lbs. per plot were examined by the authors, from time to time, for a period of over 5 months during the life of a crop of ragi (*Eleucine coracana*) raised on the plots. A number of samples were collected from each plot to a depth of 6″ and the different samples thus collected from each plot, at one time, were mixed together and treated as a whole specimen. They were then examined for their total nitrogen contents according to the method of Sreenivasan (1932) (Table III).

TABLE III.

Nitrogen distribution in soil plots.

Plot	Date of sampling						Mean and standard deviation
	18th Sep.	3rd Oct.	1st Nov.	1st Dec.	5th Jan.	4th Feb.	
	Nitrogen as p.p.m. (averages).						
A	604	553	610	613	607	585	595± 21
B	692	515	572	553	567	547	574± 56
C	552	590	560	558	570	620	575± 24
D	605	610	534	673	656	525	600± 56
E	488	483	350	542	674	645	530±108
F	539	539	612	617	548	525	563± 37
G	582	550	..	645	609	647	606± 37
H	504	656	658	528	564	558	578± 59
Mean and Std. deviation ..	571	562	557	591	599	581	
±	61	51	92	50	43	47	

The most striking observation to be noticed from the above table is the great variation in the nitrogen content existing between the various samples within each plot from time to time, and also in the different plots at the same time. Thus, taking the samples collected on 1st November, the coefficient of variability is sixteen, which means that over five-sixths of the total determinations may be expected to lie within the range on either side of the mean. In other words, the range within which five-sixth of the determinations may be expected to fall is 464 to 649 p.p.m. in this case. The extreme range would of course be much greater. In a like manner, the variations between the nitrogen figures of the same plot at different intervals of time also appears to be considerable. Thus with plot E, the mean is 530 and the standard deviation 108, *i.e.*, the coefficient of variability (C,V.) is about a fifth part.

Similar results were obtained by the authors in regard to ammonia, nitrate and organic matter contents of manured as well as unmanured plots.

From a consideration of the analytical error involved in the study of nitrogen balance in the soil, Pfeiffer and Blanck (1913) have concluded that the non-homogeneous character of the soil is itself a serious factor which would cause large differences between duplicate determinations or even successive samples. Robinson and Lloyd (1915), Waynick (1918), Prince (1923), Bear and McClure (1920) and others have also drawn attention to the existence of normal variations in the composition of the soil from point to point in the field.

It would appear, therefore, that random specimens from a field or even a uniform plot of land would not give concordant results and that a high sampling error may be expected. The values obtained for either independent specimens from the same area or for mixtures representing collections from different spots would exhibit a variation which might easily be mistaken for periodic fluctuations in the land itself.

Furthermore, the major part of the nitrogen of the soil is in organic form, being mostly derived from either added manures or plant residues decomposing in it. Since it is not possible in ordinary field practice to distribute the organic matter so evenly as to facilitate accurate sampling for analytical work, it would follow that although the total amounts of nitrogen spread over large areas may be the same, the quantities present in small samples collected as representative specimens may vary considerably. Additional error is also introduced by cattle grazing or sheep-folding during off-seasons, thus resulting in the droppings being unevenly distributed over the surface of the soil. In assessing the influence of season on processes like nitrogen fixation the effects of different external factors on the movement of different soil constituents would also require careful consideration. Thus, it is well known that during periods of fallow, a large part of the nitrogen, particularly the soluble forms, moves into the sub-soil and does not become available until the planting of the subsequent crop. During the rainy season, the finer fractions containing the highest percentage of fertilising ingredients would be washed from the surface of a sloping or uneven soil and carried to the lower regions exposing only the less rich, coarse fractions at the surface. Even on the same plot of land considerable variations in the distribution of different soil constituents can be brought about by washing or silting as the case may be.

It is generally believed that among the nitrogenous constituents of the soil, only the nitrates are capable of periodic movement from one stratum to another. In the ordinary soil, nitrates are present only in small quantities so that their movements may not lead to any considerable change in the total nitrogen content. There is evidence to show, however, that certain forms of organic nitrogen are also capable of movement through the soil. Soil albuminoids are generally insoluble in water, but they are partly peptised by dilute salt solutions. All soils contain soluble salts (though to varying extents), so that when rain or irrigation water soaks in, it dissolves the salts which, in turn, peptise a portion of the albuminoids. This action is no doubt helped

by the reaction of the soil. In soils of pH 7·5 or more, the peptising action will be more pronounced than in those of pH 7. Acidity of the soil (pH 6·5 and below) may also help to facilitate the peptisation of certain forms of nitrogen. In this manner, there may be steady movement of organic nitrogen from one stratum to another in the soil.

The quantity of organic nitrogen peptised at any one time may be comparatively small ; but repeated action, as may be naturally expected during the months of heavy and continuous rainfall, may carry down a considerable portion of the organic nitrogen to the lower strata of the soil and, if the soil conditions permit, even shift it from one locality to another. When the dry weather comes round, the saline extract, together with the albuminoids, will be carried up to the surface layers through capillary action. This would suggest that during the post-monsoon period, and especially the Spring months, the surface layers of the soil will show an appreciable gain in nitrogen. In a like manner, the nitrogen content of the surface layers of a heavily irrigated field will show an appreciable increase as soon as the watering is stopped. This is actually what happens when the crop approaches the ripening stage and the reported increase in nitrogen at the time of and shortly after harvest (and which is attributed by some workers to a possible flow-back of nitrogenous constituents from the plant) may be accounted for by this phenomenon.

The foregoing explanation may account for the apparent discrepancy between laboratory observations on the one hand and field results on the other. The laboratory experiments are generally carried out in glass or Chinaware so that the peptised nitrogen, if any, has no chance to move out of the system. There is, in consequence, no appreciable change in the total nitrogen content of the laboratory sample. On the other hand, the field samples permit of movement of nitrogen so that on taking the samples from the usual surface (0-3′) layers, one may find apparent loss of nitrogen in certain seasons and gain in others.

Further work on this aspect of the problem is already in progress and it is hoped that the results will throw some fresh light on the mechanism of periodic fluctuations in the nitrogen contents of field samples.

SUMMARY

Studies on periodic changes in nitrogen contents of soils are complicated by two factors, namely the error due to analytical methods and the error due to soil heterogeneity. The significance of these two factors as affecting the interpretation of results obtained from field data are fully considered. The former can be overcome by adopting one of the improved methods of estimating total nitrogen. The error due to field experimentation can be overcome by repeating the experiment over long periods, by multiplying the number of plots in a given field, by examination of a sufficiently large number of samples and by statistically inquiring into the mathematical error involved in such determinations.

Evidence has been adduced to show that in addition to nitrates (which are present in comparatively small quantities) organic nitrogen present in field samples may move from one stratum to another and, under favourable conditions, even laterally from one area to another. This may at least partly account for the periodic fluctuations observed in the total nitrogen contents of field samples.

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DETERMINATION OF NITROUS AND NITRIC NITROGEN IN SOILS.

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Although the importance of nitrites and nitrates in the biochemical transformations of the soil and their bearing on the physiology of the plant have been generally recognised, there are yet very few methods for the accurate determination of these two forms of nitrogen. Moreover, the methods usually adopted for the drying, storage and extraction of soil are not adequate for the stability of nitrites, so that the estimates usually obtained are very low. As the result of this, it is generally assumed that the nitrite content of the soil is negligible : indeed, very few workers of the present day make a separate estimation of that form of nitrogen.

Among the commoner methods, the best known and the one most largely used is that of Giess-Ilosvay, a colorimetric method. This is suitable only for the estimation of minute quantities of nitrites. The accuracy of estimation by this method is affected by the presence of organic matter. Among the other methods, those of Lunge, Kubel, Davisson, Robin, Winkler, Cool, and Yoe, Pandalai and Rao [1] are the most satisfactory, but they are not applicable to soils.

Nitrates are generally estimated by the phenol disulphonic method (colorimetric) as modified by Chamot, Pratt and Redfield [2]. The reduction methods of determination are also numerous. Agreeing in principle, they differ from each other chiefly in regard to the reagents employed for reduction. All of them involve the conversion of nitrate to ammonia and the subsequent determination of the ammonia. It is well known that if the soil extract contains any form of organic matter, particularly nitrogenous, there is great chance of these methods giving inaccurate results.

In view of these and the need for more quantitative information regarding the occurrence and distribution of nitrites and nitrates in soils, the present work was taken up.

I. ESTIMATION OF NITRITE.

Stabilization of nitrite in soil samples.

The method of air drying which is generally adopted leads to partial oxidation of nitrite. Storage also leads to low estimates being obtained. It is known that nitrites are unstable in acid media, moderately so under neutral conditions and quite stable in presence of free alkali. Indeed the conversion of nitrite to nitrate in solution is only a question of the pH condition of the medium. The reaction is an autocatalytic one :

$3HNO_2 = HNO_3 + 2NO + H_2O$. The nitric oxide absorbs oxygen from the air and renders the reaction continuous. Thus $2NO + H_2O + O \rightarrow HNO_2 + HNO_3$; $2HNO_2 + O_2 \rightarrow 2HNO_3$ and these go on, so that unless the medium is maintained sufficiently alkaline, the deterioration of nitrite is only a question of time. Thus, to ensure the stability of nitrites in the soil it is essential that the medium must be made alkaline. Among the alkalies, caustic soda or potash is useful but it also extracts large quantities of humic matter, which interferes with the subsequent estimations. Sodium carbonate shares the same disadvantage, though to a lesser extent. Caustic lime has been found to be a satisfactory reagent in stabilizing the nitrite present in soil samples. There is no doubt that some small quantity of organic matter is extracted by it, but that can be easily removed by subsequent treatment. In Table I are given the results of lime treatment of fresh soil samples and the results reveal the advantage of such pretreatments in preserving the nitrous nitrogen of soil samples.

TABLE I.

Effect of addition of lime on the stability of nitrite added to the soil

Treatment of soil.	Soil alone.	Soil + 10 p.p.m. of nitrite N.	Soil + 20 p.p.m. of nitrite N.	Soil + 40 p.p.m. of nitrite N.
Nitrite N as estimated after addition of lime	6·7	16·7	26·9	46·5
	6·9	16·8	26·4	46·9
Nitrite N as estimated after standing for one week with lime	6·8	16·7	26·8	47·0
	6·9	16·9	26·8	46·7

Clarification and removal of organic matter.

The alkaline extract is sometimes coloured (golden yellow) and must be specially treated to remove interfering organic matter. A number of reagents—alumina cream, charcoal, copper hydroxide, basic lead acetate, calcium carbonate, copper sulphate, potash alum—have been used for this purpose by various workers. A systematic study with several of these reagents in different combinations showed that with caustic lime, copper sulphate and basic lead acetate there was the twofold advantage in that they at once stabilised the entire quantity of the nitrous nitrogen besides clarifying and decolourising the solution. Even in the absence of lead acetate, a clear filtrate was obtained, but the filtration was very slow. The quick filtration combined with the easy washing eliminate the chances of nitrites and nitrates being retained in the precipitate. In Table II are given the results of experiments done with an extract obtained after the above treatment. 50 gm. lots of soils were treated

in each case with nitrite corresponding to 20 p.p.m. and 66 p.p.m. of nitrogen respectively and the nitrite determined by the Griess-Ilosvay colorimetric method.

TABLE II.

Effect of clarifying agents.

Description of soil sample	Clarifying agent	50 gms. soil alone	Soil + 20 p.p.m. of nitrite N.	Soil + 66 p.p.m. of nitrite N.
Bangalore, Sandy loam.	(a) Lime alone	7·6	22·9	68·5
	(b) Lime + Copper sulphate ..	7·6	23·4	73·9
	(c) Lime + Copper sulphate + Basic lead acetate ..	7·6	27·9	74·0
Dry land Soil, Nasik, Bombay.	(a) Lime alone	3·5	24·0	70
	(b) Lime + Copper sulphate ..	3·0	22·9	67
	(c) Lime + Copper sulphate + Basic lead acetate ..	3·2	23·2	69
Pyinmoona, Burma.	(a) Lime alone	nil	22	67
	(b) Lime + Copper sulphate ..	nil	22	67
	(c) Lime + Copper sulphate + Basic lead acetate ..	nil	20	66

The efficiency of the copper-lead clarifying mixture was further tested by adding certain forms of organic matter such as glucose and humic acid to the soil and testing the extract for organic carbon. In another set, the soil samples were treated with manures such as farmyard manure, hongay cake, hongay leaf, etc., and the decomposition allowed to proceed under conditions of both dry and wet cultivation. The resulting extracts were also examined for their organic carbon content. It was found, however, that in none of the cases did traces of organic matter pass into the filtrates. The latter were perfectly clear and colourless.

Estimation of nitrite by titration.—Some experiments were next carried out to determine whether the nitrite in solution can be estimated by direct titration. Four methods were tried :

      (i) Direct titration against standard permanganate ;

     (ii) indirect titration against permanganate after addition of excess of acidified hydrogen peroxide ;

   (iii) addition of excess of permanganate and back titrating the unused permanganate against ferrous ammonium sulphate ;

   (iv) addition of excess of permanganate and determining the unused permanganate iodimetrically.

Table III gives the results of these experiments. It may be noted that direct titration against permanganate did not yield accurate results. This confirms the observations of previous workers (Cool and Yoe, *loc. cit.* ; Pandalai and Rao, *loc. cit.*)

TABLE III.

Soil and Treatment		Method employed			
		i	ii	iii	iv
Bangalore Soil.	Soil alone	7·8	6·4	6·9	6·5
	Soil + 10 p.p.m. of nitrite N.	18	16·6	17·0	16·6
	Soil + 33 p.p.m. of nitrite N.	42	39·5	40·0	39·7
Peaty soil, Travancore.	Soil alone	30	24·0	25	24·2
	Soil + 10 p.p.m. of nitrite N.	43	34·8	35·9	34·8
	Soil + 33 p.p.m. of nitrite N.	64	63·2	60·0	63·7
Willingdon Farm Pasture plot.	Soil alone	*nil*	*nil*	*nil*	*nil*
	Soil + 10 p.p.m. of nitrite N.	10·5	10·1	10·2	10·0
	Soil + 33 p.p.m. of nitrite N.	33·8	33·4	33·4	33·2

Addition of excess of acidified hydrogen peroxide and the titration of the unused peroxide proved a very satisfactory method. It must be emphasised, however, that all precautions have to be taken to prevent the deterioration of the hydrogen peroxide solution and to avoid its decomposition by surface catalytic action. Quick titration is another factor to be attended to. The determination of the nitrite by its oxidation by excess of permanganate and the titration of unused permanganate, either by ferrous ammonium sulphate or iodimetrically, also gave satisfactory results, though, in certain cases, the ferrous ammonium sulphate was found to be an unreliable reagent for practical purposes. On the whole, the method (ii) outlined above is very reliable and gives accurate estimates with different kinds of soils.

Oxidation of nitrite by potassium dichromate.—Since dichromate is a more stable reagent than permanganate and since the chances of its reacting with organic matter are small, it was thought worth while to try to use dichromate for oxidising the nitrite in the extract. If a known excess is used, the balance after oxidation can be determined iodimetrically. The results in Table IV show that dichromate is without action on cold nitrite, and that the mixture has to be heated at least to 80°C. before any reaction can commence. Even at higher temperatures, the heating has to be continued for some time before the reaction can proceed to completion.

TABLE IV.

Effect of temperature on the oxidation of nitrite by an acid solution of potassium dichromate.

Heated for 10 minutes at	Nitrite N. as estimated* (in mg.)	Nitrite as estimated† (in mg.)
30°	*nil*	*nil*
40°	6·79	12·86
50°	5·03	13·50
60°	6·79	13·89
70°	6·79	13·76
·80°	5·27	14·02
90°	5·29	13·50
100°	5·47	13·50
Boiling vigorously ..	5·29	13·50

It is thus seen that conditions are yet to be standardised under which the oxidation of nitrite by acidified dichromate solution can take place quantitatively. Now, even if it were possible to make the reaction quantitative, there would still have been the inherent difficulty of heating the solution and cooling it, the whole process being very tedious and unsuitable for routine work.

Oxidation of nitrite by hydrogen peroxide.—There are numerous references to show that nitrites are quantitatively oxidised in acid solutions to nitrates by hydrogen peroxide and that the oxidation is instantaneous. Some experiments were done first with pure sodium nitrite solutions and then with soil extracts to which nitrite solutions were added. The solutions were made just acidic and a known excess of the peroxide added (30% Gewichte perhydrol from E. Merck) followed immediately by a large excess of sulphuric acid (1 : 1). The solution was shaken well and forthwith titrated against standard permanganate. The results of a few experiments are given in Table V. The method works very satisfactorily both with pure solutions and soil extracts. A blank determination with all the reagents and with the soil sample should be done. It was found that, by adopting constancy of conditions and careful avoidance of factors which bring about the decomposition of hydrogen peroxide, excellent results of an easily reproducible nature could be got. The only difficulty, however, is in maintaining a stock solution of hydrogen peroxide but it is now well known that a hydrogen peroxide solution in normal sulphuric acid is perfectly stable for 3 weeks. Nevertheless, either freshly prepared solutions or frequent standardisation of stored solutions are desirable as safeguards.

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* Expected value, 7·44 mg.   † Expected value, 14·02 mg.

TABLE V.

Source of nitrite nitrogen	Nitrite nitrogen estimated after necessary correction for blank in the case of soils		Percentage oxidation
	Added (in mg.)	Found (in mg.)	
Pure sodium nitrite	6·9	6·9	100
	6·9	6·9	100
	13·8	13·8	100
	13·8	13·5	98
Pure nitrite added to 50 gms. of black cotton soil.	6·9	6·8	98·5
	6·9	6·7	97·1
	13·8	13·2	95·6
	13·8	13·8	100
	13·8	13·8	100
Dry land soil, Nasik, Bombay	6·9	6·8	98·5
	13·8	13·7	99·2
Kari soil, Travancore	6·9	6·4	92·8
	13·8	13·5	98·0
Sandy loam, Bangalore	6·9	6·9	100
	6·9	6·8	98·5
	13·8	13·8	100
	13·8	13·8	100

General procedure for estimation of nitrites.—Based on the foregoing observations, the following procedure has been developed. The soil (50 gms. ; wet or dry) is treated with 30–40 c.c. of caustic lime (50 per cent suspension) and sufficient quantity of water to bring it up to a homogeneous suspension. The latter is well stirred and then treated with 2–4 c.c. of copper sulphate (10 per cent solution) and basic lead acetate (1 to 3 c.c. of a 10 per cent solution) respectively. More water is added if necessary and the suspension again well stirred and filtered through Buchner. The filtrate which should be clear and colourless is then treated with standard permanganate in excess followed by dilute sulphuric acid in excess. The mixture is well shaken and then treated with potassium iodide (2 to 5 c.c. of a 10 per cent solution). The iodine liberated is titrated against standard thiosulphate (0·05 N) in the usual way.

In the case of wet soils, the general procedure will be the same except that the moisture will have to be determined on a separate sample and the calculation made in the usual way.

Nitrite estimation in some Indian soils.—Applying the procedure detailed above, the nitrite content of some representative Indian soils (air dried samples) were determined. The results are presented in Table VI. In each case nitrite nitrogen amounting to 70 p.p.m. was added in the form of sodium nitrite solution and the values given in each case indicate the nitrite nitrogen recovered by the respective methods (after correction for the actual nitrite content of the soils).

TABLE VI

Nitrite contents of some Indian soils

Description of soil	Nitrite (in p.p.m.) as estimated by the Griess-Ilosvay method	Nitrite (in p.p.m.) as estimated by the new method	Description of soil	Nitrite (in p.p.m.) as estimated by the Griess-Ilosvay method	Nitrite (in p.p.m.) as estimated by the new method
Red sandy loam, Bangalore	69	70	Alluvial soil, Travancore	64	70
Dry land soil, Nasik, Bombay	69	69·5	Upland farm, Cuttack	69	69·5
Kari soil, Travancore	65	70·4	Pasture Plot, Wellington Farm	69	70
Calcareous soil, N. Bihar	69	70	Upland soil, N. Bihar	69	69·9
Govt. Wheat Farm, Jacobabad	68	68·9	Black cotton soil, Nagpur	68	70
Wheat and sugar-cane soil, Punjab	66·4	69·5	Burma, Pyinmcona	66	69·5

There was very close agreement between the duplicate values obtained by the new method. The average values (as may be seen from the above) were also higher than those obtained by the Griess-Ilosvay method. In the new method there is the added advantage that the estimation can be carried out with fairly large quantities of soil so that the chances of error through sampling are greatly reduced.

It may be mentioned, however, that in ordinary practice it would be desirable to estimate nitrite on the fresh sample. If the determination cannot be carried out immediately, the soil should be treated with calcium hydroxide and the wet suspension stored as such until the estimation can be taken up. As is well known, drying leads to oxidation of a part of nitrite, so that the estimates as obtained on air dried specimens do not generally convey a correct idea of the original nitrite contents of soils.

Although the procedure adopted for clarification is efficient in removing humic matter and interfering albuminoid substances, it still appeared probable that a few soluble forms of organic matter may pass into the filtrate and interfere with the accuracy of the estimation. Among these, amides and amino

acids may be reasonably expected.   In the previous experiments, where freshly
decomposing forms of organic matter were added to the soil, it was observed
that not even a trace of any organic carbon passed into the filtrate.   Experiments with urea and glycine up to a concentration of 10 p.p.m. of nitrogen
showed that these substances did not interfere with the estimation.   Addition
of fairly large amounts, however, did interfere with the accuracy of the estimation, but such quantities do not ordinarily exist in any soil.

II.   Determination of Nitrate.

Nitrates are generally extracted together with nitrites and, as the extracts
are practically free from organic matter, the same samples can also be used
for the determination of nitrates.   The estimation may be carried out either
on separate portions of the extract or on the same sample.   In both the
cases, the estimate will represent the combined nitrite and nitrate nitrogen.
By a separate determination of the former, the latter can be calculated.

In the usual procedure for the estimation of nitrates by titrimetric method,
all interfering organic substances have to be destroyed by oxidation.   It is
generally recognised that destruction of organic matter by reagents such as
alkaline permanganate is extremely slow and tedious, prolonged boiling for
several hours being required in many cases.   The subsequent reduction of
nitrate to ammonia especially in alkaline medium is very inconvenient and
often requires redistillation.   The most efficient reducing agents such as
aluminium or Devarda's alloy are so vigorous in their reaction that the alkali
is mechanically carried over as spray during distillation.   The procedure
described below eliminates both the above mentioned defects.

The aqueous extract of soil obtained in the manner described above
is treated with caustic alkali solution in excess and boiled for about five minutes,
to remove traces of ammonia which may be present.   It is then cooled and
distilled with Devarda's alloy.   The reduction goes on smoothly and to
completion.   This is traceable to the small quantities of the lead salt originally
added as the clarifying agent.   A thin coat of lead is formed around the reducing
agent and thus mitigates the vigour of the action.   Addition of large quantities of lead to the extract will no doubt lead to the formation of thicker
coats of lead around the alloy and thus prevent interaction with the alkali,
but the small quantities such as are present in the soil extract helps to moderate
the reaction without impairing the efficiency.

The above observations are of considerable practical interest.   In the
usual procedure for the estimation of nitrates by reduction with Devarda's
alloy or aluminium, the distillation has to be carried out slowly and with
considerable care.   Even then it is difficult to prevent traces of alkali being
mechanically carried over into the distillate.   Addition of small quantity of a
lead salt, preferably the acetate (1–3 c.c. of a 10 per cent solution) is highly
effective in eliminating this defect.   In place of the lead salt any other metal

which can displace aluminium or zinc can be used. The following are some of
the results obtained by the modified procedure (Table VII) when applied to a
few representative Indian soils. In each case, nitrate nitrogen amounting to
70 p.p.m. was added in the form of a potassium nitrate solution and the values
given in the table indicate the nitrate nitrogen recovered in each case by the
respective methods (after correction for the actual nitrate contents of the
soil).

TABLE VII.

Description of soil sample	Phenol disulphonic acid method after clarification	Devarda's alloy method	The procedure described in this paper	Description of soil sample	Phenol disulphonic acid method after clarification	Devarda's alloy method	The procedure described in this paper
	NITRATE NITROGEN IN PARTS PER MILLION AS ESTIMATED BY						
Dry land soil, Nasik, Bombay ..	74 / 72	73 / 74	71 / 71	Upland soil, Cuttack	70·07 / 68·80	71 / 71	70 / 70
Calcareous soil, N. Bihar.	72 / 72	73 / 72	71 / 72	Wellington Farm, Pasture Plot.	71 / 70	72 / 73	71 / 71
Alluvial soil, Travancore.	70 / 72	70 / 73	71 / 72	Black cotton soil, Nagpur.	69	71	70
Red sandy loam, Bangalore.	70 / 71	72 / 73	71 / 71	Khamba village, surface soil, Ahmedabad.	72 / 73	73 / 74	72 / 72
Kari soil, Travancore	74 / 73 / 75	76 / 75 / 76	75 / 75 / 75	Upland soil, Gorakhpur.	70 / 69	71 / 71	70 / 70
Wheat and sugarcane soil, Punjab.	68 / 68	69 / 69	67·5 / 68·5	Pyinmeona, Burma	68·9 / 69·0	72 / 74	68·9 / 68·9
				Upland soil, N. Bihar	69·0 / 70·0	70 / 72	70·0 / 69·8

The advantages of the procedure described above may be enumerated as
follows :—(1) The entire quantity of the nitrite present in the soil system can
be extracted. (2) The filtration of the extract is very rapid : the filtrate is
colourless and completely free from organic matter. (3) The nitrate can be
easily estimated by an accurate method of volumetric titration where the
chances of error are at a minimum. (4) The extract can be used either as such
or after estimation of nitrite for the determination of nitrate as there is no
interfering organic matter. (5) The entire procedure including extraction,
filtration and the final estimation can be carried out in 1½ to 2 hours so that

with three or four sets of apparatus a large number of determinations can be completed in the course of an average working day.

SUMMARY.

(1) A direct volumetric method for the estimation of nitrite and nitrate in the same sample has been described. By pretreating the soil with a small quantity of slaked lime the nitrite is first stabilised. By adding a clarifying mixture consisting of copper sulphate and lead acetate together with excess of slaked lime, organic matter and other interfering substances are removed. The nitrite in the filtrate is estimated by addition of excess of permanganate or hydrogen peroxide (in acid solution) and back titrating the unused portion.

(2) The procedure can be extended to include nitrates. An aliquot of the aqueous extract is boiled with alkaline permanganate for a few minutes and then distilled with Devarda's alloy or aluminium in the usual way. The small quantity of lead present in the extract forms a light coat around the reducing agent and thus renders the distillation smooth without impairing the efficiency of reduction.

(3) The methods described above have been utilised for the determinations of nitrites and nitrates in a number of tropical soils. It is also eminently suitable for the study of the changes in different seasons and at various stages both before and after manuring. It can be applied to the study of nitrogen transformations in the swamp soil, especially in the earlier stages of puddling when the conditions are favourable for the reduction of nitrate.

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AN IMPROVED METHOD OF ESTIMATING NITROGEN IN SOILS AND PLANT MATERIALS.

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The importance of the determination of nitrogen, as an item of analytical procedure in agricultural and allied biochemical researches, has been recognised for a long time. In the study of plants, animals or microorganisms ; in the evaluation of foods, feeding stuffs, and fertilisers ; in the examination of water, sewage and soil, it is an essential operation without which no useful conclusions can be drawn. It will be no exaggeration to state that in pure research alone (apart from routine estimations which are not published) several millions of nitrogen determinations are being carried out annually in different parts of the world.

A considerable amount of attention has, therefore, been devoted, during the past fifty years, to the development of rapid and accurate methods for the determination of nitrogen. Of the several methods that have been proposed, the one originally developed by Kjeldahl (1883) and subsequently modified by Arnold (1887), Gunning (1889) and others, is the best known and has found the most favour with scientific workers. The procedure is, however, slow and tedious, especially when resistent materials of the type of soils, cereal husks and yeasts have to be digested. Besides, it presents a very objectionable feature—the production of acid fumes—necessitating the digestion being conducted in a fume chamber.

Digestion with concentrated sulphuric acid was considered to be quantitative till Bal (1925), working with the Black Cotton soils of the Central Provinces (India), showed that the results thus obtained were low and discordant. He also found that pre-treating the soil with water[1] greatly improved the conditions, facilitating smoother and quicker digestion and yielding higher and more concordant results.

Sreenivasan (1932, 1933, 1934) confirmed Bal's findings and further showed that it applied to other types of soils as well. The low values obtained by 'dry' digestion (with concentrated sulphuric acid) have been shown to be due to the formation of impenetrable protective coats of silica around undigested soil particles. Pre-treatment with water or dilute (1 : 1) acid prevents

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[1] Some recent workers (Martin and Griffith, *J.S.C.I.,* 1935, **54,** 234T ; Walkley, *J. Agric. Sci.,* 1935, **25,** 398) have recognised the advantages of pre-treatment with water.

the formation of such coats and facilitates easy penetration, so that the soil is fully digested by the acid. The 'wet' digestion can be greatly accelerated by the addition of small quantities of oxidising agents like hydrogen peroxide.

Marking, as it does, a very important advance in the field of analytical chemistry, still the 'wet' digestion has not got over the chief objectionable feature in the original Kjeldahl method, viz., the emission of acid fumes. It is because of this reason, and the possibility of conducting carbon and nitrogen determinations on the same sample, that the sulphuro-chromic acid digestion has attracted the attention of many workers, especially during the past few years.

The results obtained by some of the previous workers (Anderson and Schutte, 1924 ; Brown, 1925 ; Tiurin, 1933 ; Robertson and Shewan, 1935) with the residue after sulphuro-chromic acid digestion for organic carbon have been very discordant. In view of these divergent results, a critical re-examination of the problem was undertaken by the present authors.

Narayanayya and Subrahmanyan (1935) have shown that direct distillation of the chromic acid digest (such as that left after wet combustion for organic carbon) with alkali gives low values for nitrogen and that better estimates can be obtained by treating the residue with reducing agents such as zinc or reduced iron prior to distillation. They have also shown that chlorides present in the material to be digested cause loss of nitrogen probably due to the interaction of hypochlorous acid and ammonia. The addition of mercuric oxide has been found to overcome this defect. Based on these observations, they have outlined a method for the determination of nitrogen by chromo-sulphuric acid digestion.

The recent researches of Shewan (loc. cit.), Acharya (1935, 1936) and the present authors (1935, 1936) have shown that there is loss of nitrogen if the chromo-sulphuric acid digestion is carried out in the usual manner. When the soil is heated continuously with dichromate, water and acid—especially when the initial heating is slow and the digesting mixture is not properly refluxed—the values for nitrogen thus obtained are lower than those secured by the Kjeldahl method. This loss has been traced by us to the intermediary formation and subsequent decomposition of ammonium dichromate :—

$$(NH_4)_2SO_4 + K_2Cr_2O_7 \longrightarrow (NH_4)_2Cr_2O_7 + K_2SO_4$$
$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O.$$
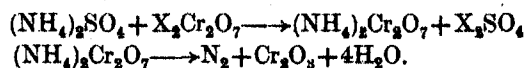
This observation is supported by direct experiments with ammonium sulphate and potassium dichromate as also with ammonium dichromate in sulphuric acid media. The formation and subsequent decomposition of ammonium dichromate occur when the potassium dichromate (or chromic anhydride) is added to a cold or moderately hot mixture of soil, acid and water. If, on the other hand, the oxidising agent is added to the boiling mixture of soil and acid and the heating is resumed immediately, the intermediate compound is not formed and, consequently, there is no loss of nitrogen Table I).

TABLE I.

Effect of addition of dichromate at different stages.

Soil from	Total Nitrogen in parts per million			Expected (Kjeldahl 'wet' digestion)
	Pre-heating to			
	No pre-heating (control)	80°	Boiling	
Tanjore	779	786	793	793
Nilgiris	1722	1767	1818	1816
Kandy	1700	1715	1766	1764

Based on the above observations, we have developed the following procedure for the determination of nitrogen in soils and biological materials. A known amount of the material to be digested is placed in a flat or round-bottomed flask—preferably the one which is to be used subsequently for the distillation—with 2 g. of mercuric oxide (red or yellow variety), 15–20 c.c. of distilled water and 40 c.c. of pure concentrated sulphuric acid. The flask is fitted with an air or water-cooled condenser, and the mixture raised to boil. After boiling for a minute or two, the flame is momentarily removed and 5 g. of potassium dichromate (or the equivalent quantity of chromic acid) are added to the mixture. The heating is resumed immediately and continued for a further period of 30 minutes. The contents of the flask are allowed to cool for about 5 minutes (without removing the condenser), then diluted to about 300 c.c. with distilled water, and reduced by excess of sodium sulphite until a black scum is formed. The mixture is then boiled for a few minutes after which zinc (about 2 g.) is added and the boiling continued for a further period of about 5 minutes. It is then cooled and distilled with excess of alkali in the usual way.

The method has been applied to the determination of the nitrogen contents of various Indian soils and commoner biological materials. The results have been given in Tables II and III.

It has been found (Harihara Iyer and Rajagopalan, 1936) that the estimates obtained by the new method include not only organic nitrogen but also nitrate up to 300 parts per million. Since most soils or biological materials contain only minute quantities of nitrates, the method is quite suitable for the estimation of total nitrogen in such materials. In this connection, the behaviour of zinc as a reducing agent is of special interest. In ordinary acid media zinc reduces nitrates to nitrites, which, on heating, are decomposed resulting in loss of nitrogen (as nitrous fumes—NO_2 and NO) from the medium. After pre-treatment with sulphite, however, and in presence of chromium salts,

TABLE II.

Description of soil	Total Nitrogen in parts per million	
	Expected*	Found
Sind (Willingdon Cattle Farm)—Alkali soil—green manured ..	520	522
Tanjore (Madras)—deltaic area—alluvial—surface	793	793
Nandyal (Madras)—red clay—surface	296	296
Cuttack (Orissa)—upland—surface	399	402
Gaya (S. Bihar)—lowland, paddy—surface	451	451
Jacobabad—Govt. wheat farm—surface..	397	394
Tindivanam (Madras)—dry land—surface	138	138
Gorakhpur—lowland—surface	848	850
N. Bihar—paddy land—surface	643	640
Devarshola (Nilgiris)—estate—surface	1,819	1,821
Kandy (Ceylon)—paddy land—sub-soil	1,769	1,767
Dharwar (Bombay)—old area—sub-soil	537	537
Sholapur—heavy black—surface	244	242
Jaffna (Ceylon)—sub-soil	397	399
Dacca—highland—cultivated—sub-soil	700.	702
Chirakkal—sandy loam—surface	315	315
Travancore—alluvial—surface	1,972	1,973
Sind—uncultivated—surface	352	350
Bangalore—gravelly soil—surface	850	850
Nagpur—black cotton—surface	420	422
Mandalay (Burma)—paddy—sub-soil	339	340
Punjab—Barani area—sub-soil	542	542
Ahmedabad—Kambha village—sub-soil.. ..	394	397
Chota Nagpur—laterite—sub-soil	209	209
Belgaum—cultivated—sub-soil	466	466

TABLE III.

Material	Total Nitrogen per cent.	
	Expected†	Found
Cyanamide	16·51	16·50
Dried Blood	12·38	12·41
Groundnut cake	7·72	7·68
Lantana leaf	2·80	2·81
Paddy husk	0·27	0·27
Ragi straw	0·52	0·52
Yeast	5·65	5·65

* Including nitrates (Sreenivasan, *J. Ind. Inst. Sci.*, 1935, **18A**, 25).
† Sreenivasan, *Ind. Jour. Agric. Soc.*, 1932, **2**, 525.

there is practically no loss of nitrogen.   This is traceable to the interaction of hydrogen sulphide (resulting from the reduction of minute quantities of sulphur dioxide left in the medium) with any nitrite that may be formed, yielding hydroxyalmine and ammonia.

Hydroxylamine combines with the chromium in the digest and is thus prevented from interaction with any fresh nitrous acid that may be formed. The products are finally reduced quantitatively to ammonia, so that there is no loss of nitrogen from the medium.   In Table IV are given some results which will show how added nitrates can be estimated, fairly accurately, by the new method.

TABLE IV.

Description of Soil		Soil alone	Soil+Nitrate (as p.p.m. of nitrogen)					
			50	100	150	200	250	300
Nagpur—Black cotton	..	428	475	520	569	632	680	721
Bangalore—gravelly soil	..	552	600	654	700	749	798	850
Mandalay—alluvial	..	340	387	440	486	544	582	636

A comparative study (Figs. 1 and 2) of the rates of digestion of soils by the different methods shows that the chromo-sulphuric acid digestion is extremely rapid, more than 95 per cent being digested in the first five minutes.   The digestion of the remaining part is generally complete in under 20 minutes and in no case is it necessary to continue the heating beyond 30 minutes.   Wet digestion, supplemented by hydrogen peroxide, follows next in order, the digestion being complete in 1½ to 2 hours.   Pre-treatment with 1 : 1 acid followed by the usual Kjeldahl digestion is complete in under 2½ hours.   The official Kjeldahl (dry) digestion is generally incomplete even at the end of 4 hours.   The estimates finally obtained by that method are also lower than those secured by the other methods.

The procedure is quite simple and rapid.   As no fumes are evolved, the digestion can be conducted at the working table itself.   Given a number of distilling sets, an average worker can complete over two dozen determinations in the course of a working day—an achievement which would be impossible by any of the other known methods.

A further advantage of the chromo-sulphuric acid method lies in the fact that it can be combined with the determination of carbon.   We have indeed shown, in a recent communication (1936), how, with a modified type of apparatus, carbonate, organic carbon and total nitrogen can be estimated in the same sample.   Such an elegant and rapid procedure is of great advantage, especially in the study of problems relating to the carbon and nitrogen transformations in soils and biological media.
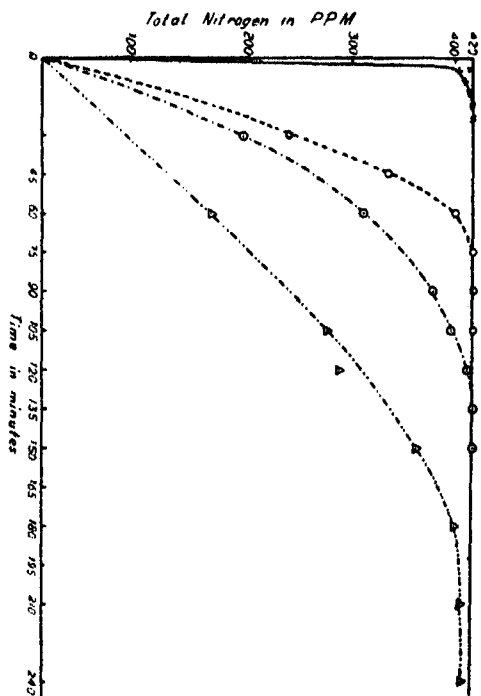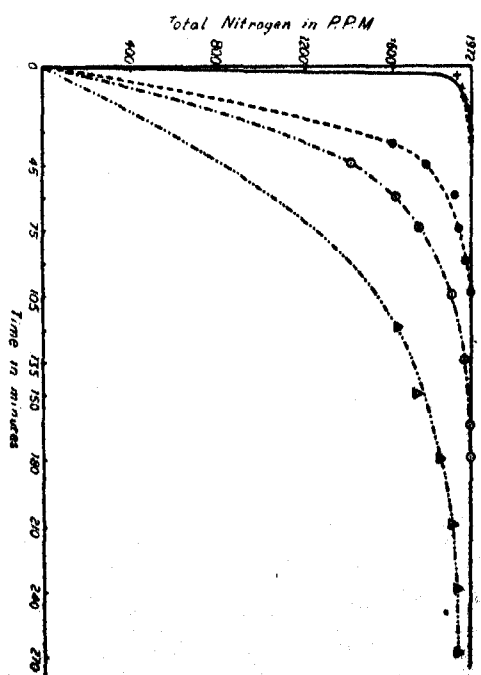
Fig 1 Rate of digestion of black cotton soil from Nagpur

Fig 2 Rate of digestion of alluvial soil from Travancore

Figs 1 and 2 Comparative efficiencies of digestion by different methods

Values obtained by fumeless digestion

— wet digestion
●—● ,, ,, wet digestion with H_2O_2
○—○ ,, ,, ,, ,, ,, H_2O
△—△ ,, ,, dry digestion (official method)

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THE NITROGEN STATUS OF THE SOILS OF BURMA.

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INTRODUCTORY.

The association of nitrogen with the organic matter of the soil is so intimate that it is usual to consider a soil rich in organic matter to be also rich in nitrogen.

Soil organic matter arises from the decomposition of plant and animal residues falling on the soil. The subject has been illuminated notably by the researches of Remezov [1933] in Russia and of Waksman and his co-workers in U.S.A. The various factors which determine the character of the equilibrium product, soil organic matter, have been discussed by Waksman and Starkey [1931] and by Waksman [1936, p. 62]. Our knowledge of the organic matter of the tropics is meagre. The general principles of decomposition of organic matter may be the same in the tropics as in temperate regions. But in contrast with the temperate regions, the largest crop in the tropics is rice which is cultivated under water-logged or partially anaerobic conditions. Sufficient is known, however, to indicate that the changes which organic materials undergo in water-logged conditions are different from those under aerobic conditions.

The conditions regulating the humus content of soils in the tropics were stated by Mohr [1929] and later experimentally verified by Senstius [1930]. According to Mohr humus can accumulate only at temperatures below 25°C. in a properly aerated soil. Under water-logged conditions, however, humus can accumulate until a temperature of about 35°C. is exceeded. Jenny [1932] has also formulated a law according to which the nitrogen and organic matter content of a soil are shown to be functions of the temperature and humidity. The nitrogen content of the soil decreases exponentially with temperature. One may therefore expect low nitrogen figures for tropical soils. According to Jenny's law, the nitrogen content increases logarithmically with increasing humidity if the temperature remained constant. The advantage of a high humidity factor is however rendered negligible as temperature seems to control the nitrogen to a much greater extent. However, Jenny's law applies only to aerobic conditions. Water-logged conditions tend to accumulate organic matter as well as nitrogen, because under these conditions the microflora seem to be able to work with a much smaller amount of nitrogen than that required by them under aerobic conditions.

The Soils of Burma.

The soil receives raw organic material from the vegetation growing on it. The vegetation in turn depends on the climatic and other factors concerned, namely, rainfall, temperature, altitude, drainage, soil reaction, soil texture and so on. The first three are regional factors. So far as Burma is concerned the mean temperatures are almost uniformly high, except in the Shan Plateau where the altitude of 3,000 feet keeps down the mean temperature by several degrees. The rainfall distribution varies widely and seems to control the nature of the vegetation. Stamp and French (1929) have classified the vegetation of Burma on the basis of rainfall and altitude. The chief divisions are :—

1. The Dry Zone : Rainfall 40 in. or less. Small trees and shrubs form the natural vegetation. Cotton, millets, jowar, maize, peas and beans grow readily. Rice and sugar-cane can be grown but require irrigation. The toddy palm grows well.

2. The Region of the Monsoon Forest. The rainfall exceeds 40 in. but does not exceed 80 in. The trees are deciduous and include teak, pyinkado and other hard woods, as well as the bamboo. A great deal of the area is covered by forest but sugar-cane, rice, sesamum, tobacco and other crops are extensively grown.

3. The Delta Region or Region of Mangrove Forest. The rainfall ranges from 80 to 120 inches. Most of the land is liable to floods and marshy conditions prevail during the rains. The area near the sea and creeks carry mangrove forest cover but a very high proportion of the area is devoted to rice cultivation.

4. The Region of Evergreen Forest. The rainfall ranges from 100 to 225 inches. The trees are green throughout the year, they are often of very large size and their wood is very hard. The area is too wet for teak and pyinkado. Most of the lowlying land is cultivated. Rice is the chief crop. Rubber and mangosteens are grown on upland soils. Cocoanut palms are important near the sea.

5. The Shan Plateau. The altitude is about 3,000 feet or more. The rainfall varies from 50 to 60 inches. The soil is a red loam derived from dolomitic limestone and other hard rocks. On the hills there are evergreen forests consisting of oaks and pines. On flat or rolling land grass is the chief vegetation. Rice is cultivated in the valleys but the area is well suited for the growth of coffee, tung oil tree, oranges, pears and other fruits, vegetables and a large variety of flowers. In contrast to most of the soils of the alluvial plains of the lowlands which are generally badly drained, the soils of the Shan Plateau are well drained except perhaps in the valleys.

A general account [Aiyar, 1936] of the agriculturally important soils of Burma has been published recently. Detailed surveys have been published for the most important rice areas in Burma [Charlton, 1931 (*a*), 1931 (*b*)] as well as for sugar-cane [Charlton, 1935]. An important monograph on the vegetation and soils of a large monsoon forest area is also available [Barrington, 1931]. Besides these, the reports of the agricultural farms, the season and crop reports, the Gazetteer of Burma, and the Atlas of Burma are useful sources of information.

The Nitrogen Content of the Soils of Burma (Table I).

Since the humus and nitrogen contents of a soil depend upon the vegetation the soils are grouped below on the basis of the vegetation groups. The rainfall and the pH values are also tabulated. The pH is a useful guide as it may indicate whether a soil contains appreciable amounts of lime or whether the soil is so acid as to suppress the bacteria and encourage the fungi. The texture of the soil may be expected to modify the rate of humus formation by regulating drainage and aeration. The value of the texture is stated in terms of the sum of the percentages of clay and silt (Atterberg) or of clay and fine silt (British). Although there are objections to this method, it is probably as good as any other.

TABLE I.

The Nitrogen Contents of the Soils of Burma

Locality	Crops	Rain-fall in inches	pH	C%	N%	Texture
The Dry Zone						
Kanbalu Farm	Dry crops	40	6·1	·80	·07	35
,,	Paddy	40	6·4	·50	·04	29
Chiba Farm (irrigated)	,,	36	6·1	·39	·05	32
,,	,,	36	6·6	·25	·04	31
Padu Farm. Black soil (Marshy)	Dry crops	32	7·9	·49	·05	78
Padu Farm. Red soil (on slope)	,,	32	6·1	·23	·04	13
Nabohla-Shwebo	Paddy	30	8·0	·25	·04	92
Mandalay Farm	Dry crops	30	8·1	·40	·03	57
,, (irrigated)	Paddy	30	8·1	·42	·04	56
Singaing—Bad drainage	Sugarcane	30	7·3	·92	·13	67
Meiktila Forest	Trees	30	7·3	·92	·03	4
Mahlaing Farm	Cotton	33	7·7	·41	·06	8
Allanmyo Farm	Dry crops	46	5·9	·82	·09	46
Tatkon Farm	,,	40	7·0	·55	·08	18
Pyawbwe	,,	32	7·8	·54	·06	43
Pwinbyu Farm	Sugarcane	35	7·3	·74	·13	68
Mean value		35	7·1	·54	·06	44

Locality	Crops	Rain-fall in inches	pH	C%	N%	Texture
The Monsoon Forest Region						
Sahmaw Estate	Virgin land Grass.	95	6·7	3·59	·29	45
,, (high land)	Sugarcane ..	95	6·4	1·92	·12	46
,, (medium)	,, ..	95	6·3	2·33	·16	25
,, (low, bad drainage)	,,	95	6·2	3·04	·21	32
Hopin (high land) ..	,, ..	90	6·6	·75	·08	23
,, (low land) ..	,, ..	90	6·5	·91	·08	31
Mawkin—						
Myitkyina Dist.	,, ..	80	4·8	2·28	·16	69
Namti ,, ..	,, ..	90	5·0	2·67	·19	47
Kondan ,, ..	,, ..	90	6·2	0·31	·03	12
Namkwin ,, ..	,, ..	90	5·7	1·39	·10	31
Mawhan—						
Myitkyina Dist.	,, ..	90	4·2	1·65	·18	57
Katha—Katha Dist. ..	,, ..	60	5·6	1·03	·09	33
Naba— ,, ..	,, ..	70	5·2	1·07	·11	25
Pyinmana Farm —						
highest land	,, ..	56	6·5	·57	·07	32
,, lowest land	,, ..	56	6·5	·74	·06	25
Monhit—Pyinmana ..	Forest	56	6·9	·99	·06	12
Thayagon ..	Sugarcane ..	56	5·9	·86	·07	43
Thabyehla ..	,, ..	56	5·1	·57	·06	27
Kanyutkwin ..	,, ..	90	5·8	1·60	·12	89
Linyawkin ..	,, ..	90	5·1	·67	·07	36
Lebyingyi ..	,, ..	90	5·9	·73	·07	35
Mean value ..		80	5·9	1·41	·11	37
The Delta Region						
Tonkan Forest Reserve	Forest ..	120	6·3	·89	·09	29
Magyipin Village ..	Paddy ..	120	6·1	1·02	·11	60
Seyokin—						
Grazing ground	Grass ..	120	6·1	·69	·05	9
Pauktaw ..	Paddy ..	120	5·9	1·56	·14	74
Pyuntaza ..	,, ..	120	6·3	1·07	·11	53
,, Reserved Forest	Trees ..	120	5·7	2·40	·20	75
Saze Village ..	Tobacco ..	120	6·1	1·00	·09	43
Thongwa—Flooded land	.. ..	120	5·9	1·23	·09	32
Kadok ..	Paddy ..	120	5·6	3·00	·24	78
Pyinbongyi ..	,, ..	120	5·2	1·10	·10	27
,, Grazing ground	Grass ..	120	5·4	1·56	·14	57
Okpo ..	Paddy ..	120	5·9	·94	·10	44
Kyaikhla—Flooded ..	,, ..	120	5·5	1·17	·09	30
Minywa ..	,, ..	120	5·7	·74	·07	25
Thanatpin—Flooded ..	,, ..	120	5·7	1·34	·13	65
Kyauktan— ,, ..	,, ..	120	5·7	·82	·07	47
Hmawbi Farm—Marshy	,, ..	96	5·6	·98	·10	85
,, Grazing ground	Grass ..	96	5·6	1·79	·16	74
,, Virgin Laterite	,, ..	96	5·1	·59	·07	24
Myaungmya Farm—						
High land	Paddy ..	99	5·3	1·86	·15	66
,, Low land ..	,, ..	99	5·5	2·23	·17	59
,, Garden soil	? ..	99	5·6	·79	·05	14
Mean value ..		114	5·7	1·28	·11	49

Locality	Crops	Rain-fall in inches	pH	C%	N%	Texture

The Evergreen Forest Regions

Locality	Crops	Rain-fall in inches	pH	C%	N%	Texture
Akyab Farm	Paddy	225	6·5	·64	·07	20
Mingan Farm (Akyab)	,,	225	5·4	1·13	·09	56
Kyaukpyu Farm—						
,, Heavy	,,	180	5·2	1·12	·10	42
,, Light ..	Cocoanut	180	5·6	·57	·05	13
Thaton—Garden soil ..	Mangosteen	217	6·1	3·05	·23	60
Mudon— ,,	,,	200	5·3	5·46	·30	61
Mudon Farm—						
Upland soil	Fruits	200	5·3	3·30	·15	60
,, Low land ..	Paddy	200	5·5	1·86	·14	50
Tavoy—Garden soil ..	Mangosteen	225	5·8	1·49	·13	89
Tenasserim—Plantation	Rubber	215	5·3	2·16	·15	26
Bilin—Plantation	,,	200	5·7	3·65	·24	52
,,	Sugarcane	200	4·2	2·24	·20	81
Hninpale	,,	200	4·3	1·01	·16	77
Shwegun (bank of Salween R)	,,	150 ?	7·1	·78	·08	34
Mean value		200	5·5	2·03	·15	52

The Soils of the Shan Plateau

Locality	Crops	Rain-fall in inches	pH	C%	N%	Texture
Yawnghwe Farm—						
Highest land	Wheat, Potatoes, Oranges	45	7·1	1·04	·09	36
,, Intermediate	,,	45	6·7	1·34	·12	47
,, Lowest	,,	45	7·9	1·90	·17	60
Heho (Valley)—						
Heavy soil	Paddy	60	8·0	5·20	·50	47
,, Red soil ..	?	60	6·3	1·65	·09	42
,, Yellow soil	?	60	5·8	·46	·11	42
Maymyo Forest						
Reserve	Trees	55	6·1	2·76	·10	60
,, (From Sylviculturist) ..	,,	55	6·6	2·54	·16	14
Taunggyi Farm	Wheat, Potatoes, Oranges	60	6·1	1·76	·14	59
Mean value		54	6·6	2·07	·16	45

N.B.—The data in the Tables refer to the surface soils.

TABLE II.

Mean Values of Nitrogen and Associated factors

Area	Rainfall	pH	C%	N%	Texture
1. The Dry Zone	35	7·1	·54	·06	44
2. The Monsoon Forest Region	80	5·9	1·41	·11	37
3. The Delta Region	114	5·7	1·28	·11	49
4. The Evergreen Forest Region	200	5·5	2·03	·15	52
5. The Shan Plateau	54	6·6	2·07	·16	45

General Remarks on the data.

The following facts are revealed by the data presented in Tables I and II :—

1. The mean nitrogen content increases with increasing rainfall [Jenny, 1932]. The slight divergence shown by the figure for the Delta Region can be explained by the fact that this area has been under cultivation for long periods.

2. The effect of temperature on nitrogen content is brought out by the striking difference between the figures for the Monsoon Forest Region and those for the Shan Plateau. The increased nitrogen content of the latter is determined by the altitude of the Plateau which ensures a lower mean temperature in this area than in the Monsoon Forest Region. Again, the nitrogen and organic matter contents of the Plateau soils are almost identical with those of the soils of the Evergreen Forest Region. Assuming a mean temperature of 22°C. for the Plateau and 28°C. for the Evergreen Forest Region, the large difference in rainfall is counterbalanced by the small difference in temperature. This fact also is in accordance with Jenny's law.

3. It has been stated by Mohr [1929], Vageler [1933] and others that the effect of water-logging a soil is to increase its organic matter and nitrogen contents. The data for the soils of Sahmaw, Pyinmana, Yawnghwe, and Myaungmya support the above view. The large organic deposits stated to occur in various parts of the tropics most probably arose under water-logged conditions.

4. The nature of the vegetation cover also has a great effect on the quantity of organic matter and nitrogen accumulated in the soil. A comparison of the data for the same place under different kinds of vegetation supports the above statement, e.g. forest, grazing land, and paddy or legumes and paddy at Kanbalu, Pyuntaza, Mudon, Bilin. The effect of cultivation in reducing the organic matter of the soil may also be inferred from the same data.

5. The texture of a soil controls the drainage and aeration. A heavy textured soil may therefore be expected to accumulate organic matter and nitrogen to a greater extent than a light textured soil. However, the mean values in Table II do not support this view, although individual comparisons from the

data in Table I seem to support it. This uncertainty is to some extent created by the manner of evaluating the texture adopted here. A value of 50 for the texture might be made up of a high proportion of clay with a little silt or the reverse. When the clay is high the drainage is much poorer than when silt is high. Apart from this, there is another point that deserves mention here. The physical properties of the clay contained in soils developed in the Dry Zone, in the Evergreen Forest Region and in the Shan Plateau would be different in all probability owing to the different climatic factors involved. The silica-sesquioxide ratio, the base exchange capacity, the lime requirement, may all give some indication of the properties of the soil clay. Even under apparently similar climatic conditions different kinds of clay, e.g. kaolin, halloysite, montmorillonite, may be produced by differences in geological parent material. Several soils of Malaya (from rubber estates) showed high percentages of clay (50 to 80 per cent) but the base exchange capacity at pH 7 seldom exceeded 10 milliequivalents per cent [Albareda]. The clays were white or only slightly brown. The probability is that these Malayan clays are mostly made up of kaolin or allied substances. The clay obtained in a mechanical analysis obviously cannot serve as a guide to the physical properties of the soil unless climatically and geologically similar areas are being considered. It would seem to be desirable to determine some suitable property of the clay in question and convert the percentage of clay by multiplying with a factor into a new value which could help in comparing the physical properties of soils generally. The silica-sesquioxide ratio may be useful but it is laborious to determine and there are also other objections which need not be discussed here.

The availability of nitrogen.

The humus present in the soil is the source of nitrogen for all crops except legumes which can utilise the nitrogen of the atmosphere. The availability of nitrogen is controlled by the decomposition of humus. The factors controlling the decomposition of humus are discussed by Waksman [1936 (b)].

The response of crops to nitrogen manuring in Burma [Watson, 1933].

The only certain method of finding out whether a soil can supply enough nitrogen for satisfactory yields of crops is to test the matter by pot and field experiments.

Paddy is the only crop that is grown throughout the country irrespective of soil and climate and the manuring of paddy has received the most attention. Of the other crops cotton and groundnut are almost confined to the Dry Zone ; sugarcane and sesamum are chiefly grown in the Monsoon Forest Region although they are cultivated to some extent in the Dry Zone.

The experiments on paddy will be considered first. The work started in 1912 at Hmawbi in the Delta and at Mandalay in the Dry Zone. Subse-

quently other stations were established and the experiments repeated, extended or modified.

The Dry Zone.—Mandalay is the chief station for paddy experiments in this area. Cattle manure, oil-cakes and sulphate of ammonia gave the largest increases in yield. Green manures and other organics have also proved excellent. Of the various synthetics, calcium cyanamide, sodium nitrate, urea, and ammonium bicarbonate have been tried and found to give low or no response. In combination with superphosphate ammonium sulphate is more effective than when they are used separately. The addition of potassium sulphate along with ammonium sulphate and super has shown no effect. Other experiments with the mixed fertilisers Leunophos, Ammophos and Nicifos showed that these are as good as a mixture of ammonium sulphate and super of similar composition.

In pot experiments Warth [1916] obtained large increases in yield of paddy by manuring with ammonium sulphate the soils of Mandalay, Tatkon, Pwinbyu, Padu and Kyaukse, all from the Dry Zone. Of these Mandalay, Padu (Black) and Kyaukse soils gave further large responses in yield when phosphate was given along with the ammonium sulphate.

A survey of the Mandalay Canal area (about 145,000 acres of irrigated paddy land) was conducted by the Agricultural Chemist. The nitrogen percentages showed only a low correlation with the yields reported [Charlton, 1931].

The Monsoon Forest Region.

Although paddy is widely grown in this region no manuring experiments have been conducted. In Warth's bulletin there is the record of a pot experiment with soil from Hopin. This soil contained 0·11 per cent of total nitrogen. In agreement with this the unmanured soil gave a high yield of paddy, in fact the highest of all the soils tried. Curiously, however, this soil also responded to ammonium sulphate to an extraordinary degree, but the addition of phosphate with the nitrogen did not materially improve the yield. The pH of a sample of soil growing paddy taken at a later date from the same place was 5·4. The conditions are said to be marshy.

The Delta Region.

Hmawbi and Myaungmya are the chief experimental stations. This is the most important paddy area. The experiments conducted at Mandalay have been duplicated at Hmawbi and in general the conclusions arrived at are the same. The response to ammonium sulphate has been higher than in Mandalay. While phosphate alone or in combination with ammonia has given good increases, potash seems to give negligible effects alone or in combination. The pot tests of Warth with Hmawbi soil showed large increases in yield of paddy by manuring with ammonium sulphate alone or in combination with super. In a further series of tests with the soils of the Delta, Warth and

Po Shin [1919] found that the phosphates applied as manure were effectively utilised by paddy only when ammonium sulphate was also given in addition.

A soil survey of the Pegu District [Charlton, 1931 (b)] (about 1 million acres) showed that there was a significant correlation between the nitrogen content of soils and the yields of paddy.

The experiments at Myaungmya have shown that large increases in paddy are obtainable by the use of Ammophos, Nicifos and similar combinations.

The Evergreen Forest Region.

Akyab and Mudon are the principal experimental Stations. Paddy is grown throughout the region wherever the land is relatively flat. At Akyab farm Leunophos gave a maximum increase of paddy with an application of 300 lb. per acre and the yield started decreasing with higher doses. At Mingan, a substation of Akyab, the increases obtained with Leunophos were of the same order as at Akyab. At Mudon the experiments were more numerous. Nicifos, Diammophos, and Leunophos gave moderate increases in yield of paddy. In combination with potassium sulphate Leunophos did not give any appreciable increases in yield over that obtained with Leunophos alone.

The Shan Plateau.

Paddy is grown chiefly in the valleys but no manuring experiments have been carried out there.

The chief facts observed in the manuring of paddy in the various areas are (1) that a good or moderate increase in yield is obtained throughout by the use of ammonium sulphate; (2) that phosphate in combination with ammonium sulphate is generally more advantageous than with ammonium sulphate alone; (3) the use of potash either alone or in combination has been of no value; (4) Organic manures always give satisfactory increases in yield.

These observations call for comment. Although paddy has a preference for ammonia as opposed to nitrate it is not clear why the use of ammonium bicarbonate does not produce the same effect as the sulphate. Urea and calcium cyanamide are also similar to the bicarbonate. On the other hand green manures and other organics ploughed into the paddy field liberate ammonia rapidly [Subrahmanyan, 1927 ; Joachim and Kandiah, 1929] and large increases in yield of paddy have been obtained in most places. Ammonium sulphate and the organic manures therefore seem to supply some substance or substances required by paddy which the other synthetics do not contain. The obvious substance would seem to be sulphur. It has been shown that the protein sulphur metabolism is related to the ammonia—nitrogen present [Heiserich, 1935]. Another possibility is that the ammonium sulphate and the organic materials liberate some element from the soil, e.g. iron which the other compounds are unable to do.

Another striking fact is the failure of potash to improve the yield of paddy. In general it is known that the assimilation of nitrate nitrogen is dependant

upon an adequate supply of potash. This may have something to do with the charge on the potassium and nitrate ions. With paddy, however, since ammonium ions are used instead of nitrate, there may be antagonism between the two positive ions. The same fact has been reported from Malaya, British Guiana, Italy and elsewhere. On the other hand, potash is always used in Spain, Hawaii and Japan which produce large yields of rice per acre.

Again there seems to be some limiting factor at work in all tropical paddy growing areas. The large increases in yield obtained in cold countries [Montesoro, 1929] by increasing doses of nitrogen can nowhere be approached in the tropics. There seems to exist a bar beyond which the yield of paddy cannot be pushed whatever be the treatment so far tried. This bar appears to be at about 3,000 lbs. per acre in Burma. The existence of such a bar in Malaya has been pointed out by Belgrave in his Reports on Paddy Manuring [Belgrave, 1934]. It has been stated that the maximum yield of rice is greater towards the northern limit of cultivation due to climatic factors [Copeland, 1924]. But there are well-authenticated spots in Burma and elsewhere in the tropics where the yields are far above the 3,000 lbs. limit. A great deal of confusion exists, however, owing to the failure to test the same high yielding paddy in all the different climatic areas in each country.

In spite of the high nitrogen and organic matter contents of the soils of colder countries like Italy, Spain, Japan and U.S.A. large applications of nitrogen have been found profitable in them in paddy cultivation.

Other crops.

The experiments in Burma have not been extensive with other crops. The manuring of sugarcane at Pyinmana has shown that ammonium sulphate is more effective than nitrate and that neither potash nor phosphate appears to be necessary.

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NITROGEN AND CARBON STATUS IN RELATION TO SOIL PRODUCTIVITY.

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Soil fertility is often gauged in terms of its nitrogen content. Indian soils are usually considered deficient in this component. The carbon content and its ratio with nitrogen are held to be related to soil fertility. Colloidal fraction and moisture holding capacity also play an important part in determining the productivity of soils.

This paper presents some interesting results obtained during the examination of certain typical soils from the tracts in Central India and Rajputana served by the Institute. During March and April, 1936, samples were collected in each region, horizon by horizon, in the soil profiles differing in fertility, both virgin and cultivated, up to a depth ranging between three and five feet. A detailed description is given of the soil profiles from each region (Appendix I) together with the normal monthly means of rainfall, percentage humidities and maximum and minimum temperatures (Figs. 1-3). The soil samples were examined for the following :—

Property	Method
1. Percentage sand-free portion and clay	.. Bouyoucos (1934).
2. Percentage carbon, nitrogen and their ratio	.. Robinson, McLean, and Williams (1929).
3. Percentage moisture holding capacity	.. Keen (1921).

The results are tabulated below :—

TABLE 1.

Composition of regional soils

Bundelkhand

A

Revenue class—Parua (Clay loam soil)

Horizon	Thickness (inches)	% on oven-dry basis			% on air-dry basis		% on oven-dry basis
		Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity
		Virgin					
1	4	0·045	0·20	4·44	56·5	19·2	33·5
2	4	0·046	0·23	5·00	66·5	27·7	38·6
3	17	0·045	0·20	4·44	72·9	27·9	44·9
4	17	0·045	0·14	3·11	75·2	28·1	47·4
5	18	0·039	0·088	2·26	68·4	28·4	42·1

TABLE 1—*concld.*

Horizon	Thickness (inches)	% on oven-dry basis			% on air-dry basis		% on oven-dry basis
		Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity
Cultivated							
1	4	0·037	0·18	4·86	71·6	26·4	32·5
2	4	0·044	0·20	4·54	66·5	27·9	40·1

B

Revenue class—Kabar (Clay soil)

Virgin

1	2	0·098	0·70	7·14	70·1	26·5	43·8
2	5	0·058	0·42	7·24	76·8	29·1	43·6
3	13	0·041	0·26	6·34	76·7	27·3	45·5
4	12	0·042	0·24	5·71	76·9	29·8	45·0
5	12	0·036	0·14	3·89	76·0	30·4	47·9
6	16	0·024	0·061	2·54	77·2	30·4	50·8

Cultivated

1	2	0·068	0·39	5·74	69·9	26·7	41·6
2	7	0·017	0·21	12·35	70·9	28·4	44·8

TABLE 2.

A

Malwa

Poor, black cotton soil (Clay soil)

Horizon	Thickness (inches)	% on oven-dry basis			% on air-dry basis		% on oven-dry basis
		Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity
Virgin							
1	6	0·050	0·32	6·40	69·4	28·5	49·9
2	12	0·038	0·26	6·84	73·2	29·4	50·2
3	6	0·047	0·29	6·17	75·3	27·8	53·6
4	12	0·039	0·22	5·64	78·0	28·2	55·4

B

Rich black cotton soil (Clay soil)

(In the vicinity of a former village site)

Hori- zon	Thickness (inches)	% on oven-dry basis			% on air-dry basis		% on oven-dry basis
		Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity

Virgin

1	3	0·145	1·13	7·79	75·3	29·7	70·1
2	9	0·079	0·63	7·97	74·7	31·2	64·9
3	12	0·051	0·43	8·43	79·4	32·9	67·7
4	16	0·053	0·33	6·24	80·5	33·3	66·6
5	20	0·048	0·39	8·12	76·5	29·0	65·5

Cultivated

1	2	0·125	1·13	9·04	76·1	31·3	65·4
2	7	0·081	0·56	6·91	75·3	25·9	65·0

C

Whitish grey adhan (Clay soil) *

Virgin

1	2	0·150	1·40	9·33	70·7	29·2	58·7
2	10	0·100	0·82	8·20	68·6	28·0	53·5
3	6	0·076	0·59	7·76	75·1	31·7	61·6
4	12	0·057	0·39	6·84	77·2	33·6	69·1
5	10	0·056	0·41	7·14	69·7	29·1	71·8
6	20	0·062	0·55	8·87	72·6	27·1	63·4

Cultivated

1	2	0·124	1·00	8·06	67·3	26·8	61·2
2	6	0·102	0·82	8·04	73·4	26·6	61·0

* Garden land usually low-lying heavily manured and intensively cultivated for generations.

TABLE 3.

Rajputana, Jaipur State

A

Alkaline (Sandy loam soil)

Hori-zon	Thickness (inches)	% on oven-dry basis			% on air-dry basis		% on oven-dry basis
		Nitrogen	Carbon	C/N ratio	Sand-free portion.	Clay	Moisture holding capacity
Cultivated							
1	6	0·039	0·18	4·62	35·8	14·4	41·2
2	9	0·037	0·17	4·59	45·4	20·4	32·5
3	15	0·040	0·13	3·25	35·0	14·8	39·8
4	15	0·032	0·092	2·87	46·4	20·4	33·2

B

Sweet (Sandy loam soil)

Cultivated

Hori-zon	Thickness (inches)	Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity
1	6	0·061	0·19	3·11	24·6	11·0	30·5
2	9	0·040	0·15	3·75	35·0	15·8	38·1
3	15	0·034	0·18	5·29	36·6	14·4	40·9
4	15	0·039	0·17	4·36	35·2	14·8	39·3

TABLE 4.

Rajputana, Bikaner State

Gang Canal Colony

A

Medium (Clay loam soil)

Hori-zon	Thickness (inches)	% on oven-dry basis			% on air-dry basis		% on oven-dry basis
		Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity
Cultivated							
1	6	0·047	0·22	4·68	45·2	17·2	33·3
2	6	0·037	0·20	5·40	48·5	19·9	38·7
3	12	0·059	0·20	3·39	47·8	19·0	38·9
4	12	0·043	0·15	3·49	43·3	17·0	36·8
5	12	0·038	0·13	3·42	43·8	16·8	36·2
6	12	0·031	0·12	3·87	44·8	18·1	36·4
7	12	0·032	0·11	3·44	48·8	18·4	38·1

B

Rich (Clay loam soil)

Horizon	Thickness (inches)	% on oven-dry basis			% on air-dry basis		% on oven-dry basis
		Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity

Cultivated

Horizon	Thickness (inches)	Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity
1	6	0·045	0·17	3·77	44·2	15·5	33·2
2	6	0·039	0·15	3·84	49·2	20·6	37·4
3	12	0·030	0·15	3·84	44·0	19·2	35·3
4	12	0·034	0·14	4·11	45·5	18·0	35·5
5	12	0·031	0·13	4·19	50·1	18·0	36·3
6	12	0·030	0·14	4·67	50·4	19·2	36·9
7	12	0·036	0·16	4·44	73·2	28·2	39·1

TABLE 5.

Rajputana, Bikaner State

Gangasarowar Colony

A

Medium (Sandy)

Horizon	Thickness (inches)	% on oven-dry basis			% on air-dry basis		% on oven-dry basis
		Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity

Virgin

Horizon	Thickness (inches)	Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity
1	5·5	0·063	0·12	1·90	11·4	4·9	28·4
2	7·5	0·089	0·12	1·35	18·0	9·5	27·2
3	7·0	0·084	0·10	1·19	21·0	10·0	30·5
4	5·3	0·081	0·16	1·98	21·0	10·5	32·8
5	5·0	0·089	0·16	1·80	21·0	9·0	32·5
6	5·0	0·102	0·09	0·88	18·9	8·4	31·3
7	4·0	0·083	0·11	1·33	18·9	8·8	31·2

B

Rich (Sandy)

Virgin

Horizon	Thickness (inches)	Nitrogen	Carbon	C/N ratio	Sand-free portion	Clay	Moisture holding capacity
1	2·7	0·019	0·14	7·37	18·9	6·3	26·8
2	11·8	0·019	0·14	7·37	24·2	10·2	31·4
3	12·0	0·018	0·08	4·44	24·8	9·8	31·1
4	10·4	0·018	0·06	3·44	23·4	9·4	31·0

The values for carbon and nitrogen content were on the whole lower than those usually found in soils in temperate regions. They also widely differed between themselves. The C/N ratios exceeded ten only for the second horizon of cultivated *kabar* land. Very low ratios predominated. No consistent relation could be found between the carbon and nitrogen contents and their ratios and the other properties determined, i.e. sand-free portion, clay and their ratio and moisture holding capacity, nor with the temperatures, humidities or rainfalls characteristic of each region (Figs. 1–3). It was the same when the percentage of carbon and nitrogen were calculated on sand-free basis. Highest values for carbon and nitrogen and narrow C/N ratios were not confined to the surface horizons, most influenced by light and temperature. It seems hazardous to predict the productivity of these soils from such values. This is supported by the results of lysimeter experiments at Indore in 1933. The same cotton varieties were grown under the same conditions in lysimeters containing profile blocks of the sandy Jaipur soil, Badnawar (Dhar) whitish grey *adhan* soil and Indore medium black cotton soil.

The yields are given below :—

TABLE 6.

Yields of Seed-cotton in gms. in lysimeters, 1933

(Area 48 sq. ft.)

Variety	Jaipur profile (sandy)	Badnawar profile (whitish grey adhan)	Indore profile, Field 31. (Black cotton soil)
Cambodia Indore 1 ..	139	639	53
Malvi 9 ..	215	573	102

The carbon and nitrogen contents and their ratios in different horizons of these soils are given below :—

TABLE 7.

Percentages of carbon, nitrogen and their ratios, in the soil profiles contained in lysimeters, used for 1933 tests

Hori- son.	Jaipur profile			Badnawar profile (whitish grey adhan)			Indore profile, Field 31. (Black cotton soil)		
	Carbon	Nitro-gen	C/N ratio	Carbon	Nitro-gen	C/N ratio	Carbon	Nitro-gen	C/N ratio
1	0·15	0·053	2·83	0·54	0·11	4·90	0·38	0·069	5·50
2	0·12	0·043	2·79	0·57	0·14	4·07	0·43	0·072	5·97
3	0·19	0·047	4·04	0·38	0·18	2·10	0·40	0·059	6·79
4	0·15	0·036	4·16	0·44	0·13	3·46	0·39	0·062	6·29
5	....	....	....	0·32	0·06	3·53	0·23	0·053	4·33

The yields and nitrogen contents do not appear to be correlated.

Nitrogen deficient soils usually respond to the application of nitrogenous manures. This does not seem to be always true of these soils.

TABLE 8.

Crop-response to nitrogen on different soils. Yields of seed cotton, lbs. per acre

A

Dhar, 1934

Varieties	No treatment	Nicifos 22/18	Safflower cake	P	Sig. diff.
Malvi bulk ..	630	692	541	<0·05	126·2
Cambodia bulk ..	403	391	474	<0·05	62·2

B

Jaipur, 1934

Variety—Cambodia Indore 1

Sowing dates	Plant spacings	No treatment	Nicifos 17/45
22nd April	12″	813	949
	18″	1092	537
15th May	12″	696	537
	18″	722	337
2nd July (rains)	12″	303	305
	18″	281	313

P<0·05; Sig. diff.=329.

C

Sri Ganganagar, Bikaner State, 1934

Varieties and treatments				Manures		
Varieties	Sowing dates	Irrigation	Plant spacings	No treatment	Nicifos 17/45	Castor cake
Mollisoni	May	Moderate	12″	746	679	1031
P. 289F.	June	Moderate	6″	647	878	551
Mollisoni	June	Heavy	6″	1140	1153	1294

P<0·05; Sig. diff.=166.

Similar results have been obtained in other parts of India (Sahasrabuddhe, 1934 ; Vaidyanathan, 1934).

Dhar (1935) concluded that the C/N ratios of soils in different regions widened as the prevailing temperatures increased. Jenny (1929) drew exactly the opposite inference and found that the nitrogen contents decreased with increasing temperatures quantitatively. McLean (1930) found the C/N ratios constant for a region and that they became wider as the prevailing temperatures increased or when the soil was under grass. He did not find any consistent correlation between C/N ratios and fertility but he concluded that for soils of the same area the carbon and nitrogen content increased with fertility. He also found a consistent decrease of C/N ratio with depth in soil profiles. The data presented above show that the inferences drawn by these workers only partially represent real conditions.

The following results were obtained from a comparison of soils from patches of high and low productivity in a barley field in Jaipur and poor and rich tea soils and *patana* soils from Portswood, Ceylon :—

TABLE 9.

Nitrogen and Carbon contents and their ratios in productive and poor soils

Localities	Soils	Horizons (inches)	% Nitrogen	%· Carbon	C/N Ratio
Jaipur (1936) ..	Productive barley patch ..	{ 0 6	0·054	0·14	2·66
		{ 6 15	0·056	0·19	3·45
	Poor barley patch ..	{ 0 6	0·040	0·13	3·32
		{ 6 15	0·037	0·12	3·30
Ceylon (1935) ..	Rich tea soil ..	{ 0 6	0·620	6·17	9·95
		{ 6 15	0·460	4·21	9·15
	Poor tea soil ..	{ 0 6	0·220	1·64	7·45
		{ 6 15	0·170	1·08	6·34
	Patana tea soil ..	{ 0 6	0·520	5·34	10·26
		{ 6 15	0·340	3·94	11·59

The surface layer of the rich Ceylon tea soil gave the following results after the application of manures.

TABLE 10.

The effect of manuring of rich Ceylon tea soil on the nitrogen and carbon contents and their ratios—Ceylon, 1935

Manure	% Nitrogen	% Carbon	C/N Ratio
Applied in October, 1934—			
Green manure+pruning mixture ..	0·73	6·10	8·35
Compost	1·01	7·74	7·66
Applied in December, 1934—			
Compost	0·89	7·37	8·28

NOTE.—Samples of soils were taken in April, 1935.

The carbon-nitrogen ratio was wider for the poor patch in the same field at Jaipur, while it was narrower for poor Ceylon soil when two different soils

were compared. Similarly, between the two Ceylon soils higher carbon and nitrogen contents were found with increased fertility. Between the poor and rich patches in the same field at Jaipur they were also higher. The differences between the second horizons were much greater than those between the first. The effect of addition of carbon and nitrogen by manuring rich Ceylon tea soil, however, varied according to the manure and the interval between manuring and sampling. The wider carbon-nitrogen ratio of the *patana* soil may be the effect of being under grass or simply a field difference. Between adjacent cultivated and virgin (under grass) portions of the same field the reverse was sometimes found (Table 1A and B and Table 2B ; surface horizons of parua and rich black cotton soils and the second of *kabar*). Evidently the influence of other factors, not yet adequately studied, on the nitrogen and carbon contents in soils and their ratios interfere with the accuracy of inferences.

It appears that the absolute nitrogen and carbon contents of fertile soils may not necessarily be high because they only represent a state of equilibrium resulting from the combined action of all the external and internal factors governing the oxidation or reduction of soil organic matter—the carrier of its nitrogen. The factor actually operating is the internal environment of each horizon in the profile during the annual seasonal cycle as regards moisture, air, temperature and the dissolved material. The external climatic factors influence only indirectly just in the same way as is done by the parent rock or the adjacent horizons. Every soil thus seems to possess its own characteristic maximum possible level of carbon and nitrogen content usually reflected under virgin conditions in its surface horizon. Cultivation seems to change it even in the continuously manured *adhan* land as shown below :—

TABLE 11.

Changes in virgin soil due to cultivation

Differences between cultivated and virgin soils in	Bundelkhand				Malwa			
	Parua		Kabar		Rich		Adhan	
	Horizons							
	1	2	1	2	1	2	1	2
% Nitrogen	−0·08	−0·02	−0·03	−0·041	−0·02	+0·02	−0·026	+0·02
% Carbon	−0·02	−0·03	−0·31	−0·21	0·00	−0·07	−0·40	0·00
C/N ratio	+0·42	−0·46	−1·40	+5·11	+1·25	−1·06	−1·27	−0·16
% Sand-free portion	+15·1	0·0	−0·2	−5·9	+0·8	+0·6	−3·4	+4·8
% Clay ..	+7·2	+0·2	+0·2	−0·7	+1·6	−5·3	−2·4	−1·5
% Moisture holding capacity	−1·0	+1·5	−2·2	−1·2	−4·7	+0·1	+2·5	+7·5

Nitrogen content was lowered by cultivation in the surface horizons; the lowering appeared to be inversely proportional to the content of sand-free portion in the virgin soils.   In the second horizon nitrogen content was lowered in Bundelkhand soils in proportion to their content of sand-free portion, but in those of Malwa it rose equally for both rich and *adhan* soils.   The carbon contents were also lowered in both horizons of Bundelkhand soils, while they were lowered only in the second horizon of the rich soil and the first of the *adhan*.   The result was that the carbon-nitrogen ratio became wider in the first horizons of the *parua* and the Malwa rich soils and the second horizon of the *kabar* soil but was narrowed in the others.   Such changes were also accompanied by those in other properties.   The behaviour of the second horizon seemed to differ from that of the first, which sometimes worked in an opposite direction.   The only outstanding difference in the composition, after cultivation of the highly productive manured *adhan* land from other soils, seemed to be the narrowing of C/N ratio and increase of moisture holding capacity in *both* horizons.   It may be noted here that the second horizon of the productive patch in the Jaipur field is equally rich as the first in nitrogen and carbon.   The first two horizons of other soils did not show this degree of uniformity.

Apparently the actual differences in the content of nitrogen and carbon or their ratios necessary to increase soil productivity may be slight, as shown by the composition of the heavily manured *adhan* land.   Differences in productivity seem to depend chiefly on the extent to which the supply of nitrogen and moisture is similarly maintained by, at any rate, the first two horizons of a soil.   Wide differences between or opposite behaviour, one way or the other, of the two horizons adversely affects fertility.   Probably a prolonged existence of favourable environment during the life of the crop is a much more potent factor than anything else.

Thus, the differences in the absolute values for the nitrogen and carbon contents of soils or their ratios may not show any correlation with the differences in their fertility.   Comparisons based on them seem to have a limited value.

SUMMARY.

Nitrogen and carbon contents and their ratios for typical soils of Bundelkhand, Malwa and Rajputana were found to be low and differed widely between soils and between horizons.

Apparently no correlation existed between them and single factors like region, prevailing temperatures, rainfall, humidities, moisture holding capacities of soils, the proportion of sand-free portion, clay and their ratios.

Absolute values were usually maximum under virgin conditions in surface layers.   Cultivation changed them according to soil ' variety ' and horizon.

Even continuous application of farmyard manure did not maintain the absolute values to virgin levels.

When soil fertility is increased by the application of bulky organic manures, the differences produced in its nitrogen and carbon content may not always be as great as are found when two soils are compared.

Neither the yield of cotton in lysimeters nor its response in the field to nitrogenous manuring was proportionate to the nitrogen contents of soils used. Better crops seem to depend more on the degree of uniformity in the upper soil layers than on their nitrogen content.

Carbon and nitrogen contents represent an equilibrium reached by organic matter under the influence of the prevailing moisture, aeration, temperatures and dissolved material in the soil. Productivity increases whenever the total intake by crop-roots becomes greater.

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APPENDIX I.

Description of regional soil profiles

Region—Bundelkhand

Revenue class—Parua (Clay loam) Virgin

Horizon	Depth (inches)	Description
1.	0-4	Reddish brown colour, lumps friable, roots of grasses in abundance, gritty to touch.
2.	4-8	Similar to above, less roots, a lot of *nagar-motha* (*Cyperus scariosus*) roots.
3.	8-25	Similar to above, a few dead roots.
4.	25-42	Similar to above, very few dead roots.
5.	42-60	Similar to above.

Cultivated

1.	0-4	Similar to that of virgin soil but less lumps and roots, looser soil.
2.	4-8	Similar to virgin soil but less compact and lumps, more friable.

Revenue class—kabar (Clay soil) virgin

Horizon	Depth (inches)	Description
1.	0–2	Grey with yellowish and blackish tinge, many grass roots, small semi-friable lumps, soft to touch.
2.	2–7	Similar to above but in bigger lumps, a few *nagar-motha* roots.
3.	7–20	Colour slightly darker than the upper or lower layers, similar to above in other respects.
4	20–32	Lighter colour than the upper layer a few *kankar* nodules.
5	32–44	A lot of *kankar* nodules, colour a mixture of upper grey and lower light yellow.
6.	44–60	Colour light yellow, in other respects similar to above.

Cultivated

1.	0–2	Similar to virgin soil but slightly looser, less roots.
2.	2–7	Similar to virgin, but looser.

Region—Malwa

Poor (Clay soil), virgin

1.	0–6	Black with slight yellow tinge, a few *kankar* nodules, lumps semi-friable, a few dead roots.
2.	6–18	Similar to above with some black hard concretions (iron).
3.	18–24	Slightly more yellow, similar to above in other respects.
4.	24–36	Similar to above, *murrum* and kankar below three feet.

Rich (Clay soil), virgin

1.	0–3	Light grey, slightly loose, forming small friable lumps, large number of roots, many *kankar* nodules and a few hard, dark brown concretions (iron).
2.	3–12	Light-grey, more compact, less roots, large number of *kankar* nodules, very few dark brown concretions, chiselled face smooth and glossy.
3.	12–24	Similar to above, more compact, a few roots.
4.	24–40	Similar to above, less compact, deeper grey colour.
5.	40–60	Less compact, cleavage surface smooth and shining, tendency to form angular blocks of irregular shape, very few dark brown concretions, *kankar* nodules less than in the above, very few roots.

Cultivated

1.	0–2	Light grey, loose, small friable lumps, few dark brown concretions, *kankar* nodules, a few roots.
2.	2–9	Slightly deeper in colour, more compact forming bigger lumps, large number of small *kankar* nodules, very few roots, dark brown concretions.

Adhan (Clay soil), virgin

1.	0–2	Light grey soil, semi-friable, smooth, dark brown concretions (iron), large number of dead roots.
2.	2–12	Light grey, very few cracks, concretions similar to above, soil friable, chiselled face rough and dull.

Horizon	Depth (inches)	Description
3.	12–18	Grey colour, darker, vertical streaks, in other respects similar to above.
4.	18–30	Slightly deeper colour, streaks narrowing, similar to above in other respects.
5.	30–40	Deeper colour, chiselled face smoother, *murrum* pockets here and there.
6.	40–60	Similar to above, irregularly mottled with yellowish earth.

Cultivated

1.	0–2	Light grey, slightly whitish, ashy appearance, loose, small friable lumps, large number of dark brown concretions, very few dead roots.
2.	2–8	Semi-friable lumps, dark brown concretions, a few brick pieces, some *kankar* nodules, lighter-coloured virtical streaks, irregular vertical cracks.

Region—Rajputana, Jaipur State

Alkaline (Sandy loam soil), cultivated

1.	0–6	Yellowish brown, slightly deeper in the interior of lumps, gritty, small hard lumps, a few *kankar* nodules.
2.	6–15	Similar to above but slightly lighter colour, a few dead roots.
3.	15–30	Similar to above, but no *kankar* nodules.
4.	30–45	Lighter colour, full of stiff lumps.

Sweet (Sandy loam soil), cultivated

1.	0–6	Reddish yellow colour, lighter than the above-mentioned saline soils, no *kankar* nodules, lumps stiff, similar to above in other respects.
2.	6–15	Similar to above, a few *kankar* nodules.
3.	15–30	Similar to above, a few dead roots.
4.	30–45	Similar to above but without *kankar* nodules or dead roots.

Region—Rajputana, Gang Canal Colony, Bikaner State

Soils under cultivation since 1928

Medium (Sandy loam)

1.	0–6	Yellowish grey, gritty, full of very small friable lumps.
2.	6–12	Similar to above but slightly bigger lumps.
3.	12–24	Similar to above but slightly stiffer lumps.
4.	24–36	Similar to above but less number of lumps.
5.	36–44	Similar to above but a few *kankar* nodules.
6.	44–60	Similar to above.

Rich (Sandy loam)

The descriptions of the horizons are similar to above-mentioned medium soil except that the bottom layer (44″–60″) is softer to touch.

NOTE.—The horizons of soil in this region were not clearly demarcated in the lower depths, therefore samples were taken for every foot.

Region— Rajputana, Gangasarowar Colony, Bikaner State

Virgin soils

Medium (Sandy soil)

Horizon	Depth (inches)	Description
1.	0–5·5	Greyish yellow, no lumps, a few plant residues, some *kankar* nodules and gravel.
2.	5·5–13	Similar to above, but a few lumps.
3.	13–20	Similar to above but no lumps.
4.	20–25·3	Similar to above.
5.	25·3–30·3	Similar to above but a few hard lumps.
6.	30·3–35·3	Similar to above but a few *kankar* nodules.
7.	35·3–39·3	Same as above.

Rich (Sandy soil)

1.	0– 2·7	Greyish yellow, no lumps, small quantity of plant residues and gravel.
2.	2·7–14·5	Greyish yellow, hard lumps and plant residues (especially roots) and gravel.
3.	14·5–26·5	Greyish yellow, big lumps, dead roots, *kankar* nodules and gravel.
4.	26·5–36·9	Greyish yellow, big hard lumps, dead roots and gravel, moist soil at the bottom.

Fig. 1. Monthly normal rainfall, inches.

RAJPUTANA - BIKANER STATE.
GANGASAROWAR COLONY

RAJPUTANA - BIKANER STATE.
GANGASAROWAR COLONY

RAJPUTANA - BIKANER STATE.
GANG CANAL COLONY

RAJPUTANA - BIKANER STATE.
GANG CANAL COLONY

RAJPUTANA - JAIPUR STATE

RAJPUTANA - JAIPUR STATE.

MALWA

MALWA

BUNDELKHAND

BUNDELKHAND

MAXIMUM

MINIMUM

MONTHS - JANUARY TO DECEMBER.

MONTHS - JANUARY TO DECEMBER.
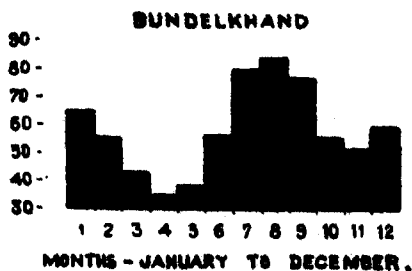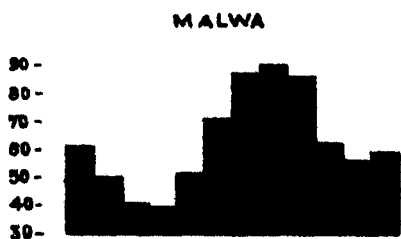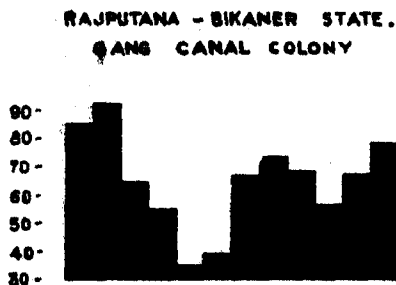
FIG. 2.   Monthly normal humidities per cent.
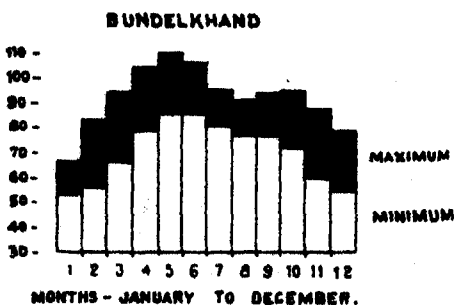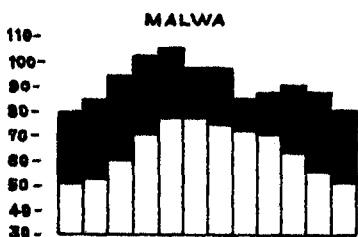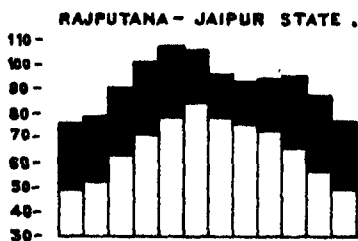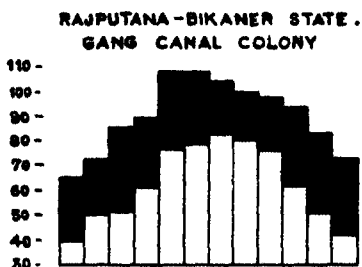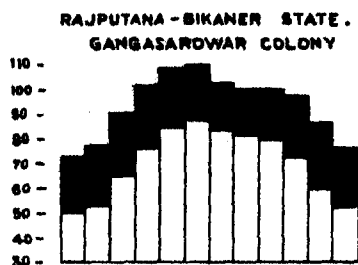
FIG. 3.   Monthly normal maximum and minimum temperature.

EXPERIMENTAL DETERMINATION OF THE ELECTRON AFFINITY OF CHLORINE.

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(Read January 5, 1937.)

It is well known that halogens have an affinity for electrons and many methods have been proposed for calculating this quantity. Let us take a halide atom X. The affinity E is given by the relation :—

$$X + e = X^- + E.$$

E can be expressed in calories, volts or wave-length units. The following table gives the values in Kilo calories obtained by different workers :—

	F	Cl	Br	I
Mayer and Helmholtz [1] (Theoretical)	95·3	86·5	81·5	74·2
J. E. Mayer [8] (Experimental)				72·6 ± 2
P. P. Sutton and J. E. Mayer [9] (Experimental)				72·4 ± 1·5
Angerer and Müller [4] (Spectroscopic)	94	86·6 } 89·6 }	79·1 } 81·3 }	71·3
E. Lederle [5] (Spectroscopic)	95 ± 2	90	82	73
Saha and Sharma [3] (Theoretical)	163·3			

There are several methods for calculating the electron affinity of the halogens. Theoretical calculations have been made by E. Mayer and L. Helmholtz [1] from the crystal energies of the alkali halides. They used the formula for the grating energy of these salts derived by Max Born and E. Mayer [2]. Saha and Sharma [3] used an extrapolation method for calculating the electron affinities. They showed that the value of the ionisation potentials of Ne-like atoms Ne, Na$^+$, Mg^{++} is given by the formula :—

$$E = (Z - 6.745)^2 + 1.917 - \frac{42.8}{(Z - 6.745)} + \frac{70.165}{(Z - 6.745)^2}.$$

If now Z is put equal to 9, we get the electron affinity for fluorine. The value so obtained is 7·1 volts ; though this value is high and is rather in violent disagreement with values calculated by other workers, it is in agreement with the value calculated by Mulliken.

On the experimental side, this subject has not been much investigated and the few data that are available have been obtained indirectly from spectroscopic methods. Only in a few cases direct experimental determination has been made. An attempt was made by Angerer and Müller [4] to calculate the electron affinity from spectroscopic evidence. They observed the absorption spectra of the vapours of alkali halides KF, NaCl, CsCl, KBr, CsBr and

KI and found that these begin to absorb continuously at high temperatures from a long wave-length limit. The continuous absorption was attributed to absorption by Cl^- or other halogen ions which was supposed to arise from thermal decomposition of the salts. The electron affinity was determined according to the quantum relation $eV = h\nu$. E. Lederle [5] calculated the electron affinities of halogens from the data of Angerer and Müller by an application of the Born-Heisenberg method, but later on H. Kuhn [6] showed that the calculation was based upon a wrong interpretation of the experimental results. Attempts have also been made to observe the emission spectra due to the capture of electrons by neutral halogen atoms, but so far nothing indicative of the actual occurrence of such a process has been observed. Oldenberg [7] tried to observe the electron-affinity spectrum with improved experimental technique, but failed to observe any new spectrum. He gave a theoretical explanation of his negative result. It amounted to showing that the probability of capture of electrons by neutral halogen atoms is very small compared to that of capture of electrons by positive ions like Na^+ leading to the formation of neutral atoms.

At the suggestion of Born and Franck, a direct method was used by J. E. Mayer [8] to determine experimentally the electron affinity of iodine. He studied the thermal ionisation of the iodides of caesium and potassium at temperatures of the order of $1160°K$. and calculated the equilibrium constant; from this, by an application of the dissociation formula and thermochemical data, he could calculate the electron affinity. Recently P. P. Sutton and J. E. Mayer [9] have described another general method for the determination of electron affinity and applied it to determine that of iodine. In Mayer and Sutton's method a tungsten filament was heated in an evacuated globe in which iodine vapour could be introduced. The iodine vapour molecules on coming into contact with the strongly heated filament suffer dissociation into atoms, some of which attract electrons and become negatively charged. These negatively charged atoms and electrons are collected by a concentric anode cylinder. By means of a magnetic field, the electrons are switched off and the current due to the negatively charged iodine atoms can be measured. The value obtained for the electron affinity of iodine was found to be $72·4 \pm 1·5$ Kilo cals. But so far no direct experimental determination on these lines of the electron affinity of the other halogens has been carried out.

The method described in this paper is also of very general application and is based on the study of the thermal ionisation of alkali halide vapours at high temperatures. The principle involved is of the same nature as that used by J. E. Mayer [8], but the experimental technique has been much improved and is altogether different.

The method essentially consists in vaporising the alkali halide in an electric furnace and then bringing it to a region of higher temperature where the vapour molecules suffer thermal dissociation into atoms as well as into ions. The products of dissociation are made to pass through a narrow circular

opening, and then through a circular diaphragm into a Faraday cylinder where they are collected and the current measured by a galvanometer.

The process of dissociation inside the high temperature region, where free electrons are also present, is given by the following set of equations· Taking sodium chloride as a typical example the possible processes of dissociation can be written as follows :—

$$NaCl \rightleftarrows Na + Cl - D \dots \quad .. \quad .. \quad .. \quad (1)$$
$$NaCl \rightleftarrows Na^+ + Cl^- - Q \quad .. \quad .. \quad .. \quad (2)$$
$$Na \rightleftarrows Na^+ + e - I \quad .. \quad .. \quad .. \quad (3)$$
$$Cl^- \rightleftarrows Cl + e - E_x \quad .. \quad .. \quad .. \quad (4)$$
$$Cl_2 \rightleftarrows 2Cl - D' \quad .. \quad .. \quad .. \quad (5)$$
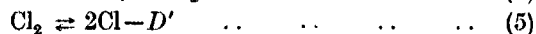
where D is the heat of dissociation of NaCl, Q the heat of dissociation into a sodium and a chlorine ion, I the ionisation potential of sodium and E the electron affinity of chlorine. D' is the heat of dissociation of chlorine into atoms. The dissociation of diatomic molecules has been studied in detail and the formula has been worked out by Gibson and Heitler [10] (see also *Treatise on Heat*, by Saha and Srivastava, p. 703, 1935) with the aid of quantum mechanics. They have taken into account the translational, rotational and vibrational states of the molecules and also the effect of nuclear spin, and given the expression for the entropy and other thermodynamical functions of diatomic molecules. If ψ be the thermodynamical potential given by the relation

$$\psi = S - \frac{U + pV}{T}$$

where U is the internal energy, S the entropy, T the absolute temperature, p the pressure and V the volume, then the expression for ψ is given by

$$\psi = -\frac{U_0}{RT} + \frac{7}{2} \ln T - \ln p + \ln \left[\frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \frac{8\pi^2 Ik}{h^2} \left\{ \frac{\frac{3}{2} + \frac{1}{2}}{\frac{1}{2}} \right\} \right] \\ - \ln \left(1 - e^{-h\nu/kT} \right) + \ln g_n$$

according as the nuclei have got a spin or not. m is the mass of the molecule, I its moment of inertia and g_n is the weight factor.

Hence, we have

$$\psi_{NaCl} = -\frac{U_{0NaCl}}{RT} + \frac{7}{2} \ln T - \ln p_{NaCl} - \ln \left(1 - e^{-h\nu/kT} \right) \\ + \ln \left[\frac{(2\pi m_{NaCl})^{3/2} k^{5/2}}{h^3} \frac{8\pi^2 Ik}{h^2} \right] + \ln g_{NaCl}$$

$$\psi_{Na} = -\frac{U_{0Na}}{RT} + \frac{5}{2} \ln T - \ln p_{Na} + \ln \frac{(2\pi m_{Na})^{3/2} k^{5/2}}{h^3} + \ln g_{Na}$$

$$\psi_{Cl} = -\frac{U_{0Cl}}{RT} + \frac{5}{2} \ln T - \ln p_{Cl} + \ln \frac{(2\pi m_{Cl})^{3/2} k^{5/2}}{h^3} + \ln g_{Cl} \ .$$

Hence $ln \dfrac{p_{Na} p_{Cl}}{p_{NaCl}} = -\dfrac{D}{RT} + \dfrac{3}{2} \, ln \, T + ln \left(1 - e^{-h\nu/kT}\right) + ln \dfrac{g_{Na} \, g_{Cl}}{g_{NaCl}}$

$$-ln \left[\frac{k^{3/2}}{2^{3/2}\pi^{1/2}Ih} \left(\frac{m_{NaCl}}{m_{Na} \, m_{Cl}} \right)^{3/2} \right].$$

Since $\psi_{NaCl} = \psi_{Na} + \psi_{Cl}$.

In this case $g_{Na} = 2$, $g_{Cl} = 4$, $g_{NaCl} = 1$

therefore, we have

$$ln \, k_1 = ln \, \frac{p_{Na} \, p_{Cl}}{p_{NaCl}} = -\frac{D}{RT} + \frac{3}{2} \, ln \, T + ln\left(1 - e^{-h\nu/kT}\right)$$

$$+ ln \left[\frac{2^{3/2}k^{3/2}}{\pi^{1/2}Ih} \left(\frac{m_{NaCl}}{m_{Na} \, m_{Cl}} \right)^{3/2} \right].$$

Similarly we have

$$ln \, k_2 = ln\frac{p_{Na} \, p_{Cl}}{p_{NaCl}} = -\frac{Q}{RT} + \frac{3}{2} \, ln \, T + ln\left(1 - e^{-h\nu/kT}\right)$$

$$+ ln \left[\frac{k^{3/2}}{2^{3/2}\pi^{1/2}Ih} \left(\frac{m_{NaCl}}{m_{Na} \, m_{Cl}} \right)^{3/2} \right].$$

Since $g_{Na^+} = 1$, $g_{Cl^-} = 1$

$$ln \, k_3 = ln \, \frac{p_{Na} \, p_e}{p_{Na}} = -\frac{I_0}{RT} + \frac{5}{2} \, ln \, T + \frac{(2\pi m_e)^{3/2}k^{5/2}}{h^3}$$

$$ln \, k_4 = ln \, \frac{p_{Cl} \, p_e}{p_{Cl^-}} = -\frac{E}{RT} + \frac{5}{2} \, ln \, T + ln \left[\frac{(2\pi m_e)^{3/2}k^{5/2}}{h^3} \right] + ln \, 8.$$

It is easy to verify that these constants are not independent, but we have

$$k_4 = \frac{k_1 \, k_3}{k_2}$$

and
$$Q = D + I - E.$$

k_2 is determined experimentally from which we can calculate the value of Q. We obtain E from the relation

$$E = D + I - Q.$$

Apparatus.—The demountable vacuum graphite furnace used in these experiments has been described in detail in a previous paper by M. N. Saha and A. N. Tandon[11]. It will suffice here only to mention the internal connections inside the furnace. These are illustrated in the adjoining diagram (Fig. 1). The high temperature is produced in the graphite tube F which is heated by passing a current of about a thousand amperes from a low tension transformer. The graphite tube has only a small hole A on one side and female cone C on the other. Into the female cone is inserted another wire-wound furnace whose male cone exactly fits C, so that the salt vapour can only pass through the hole A. The wire-wound furnace F' is so designed that the temperature of the salt vapour can be determined without much error, and the salt vapour does not condense in any part between this and

the graphite tube. An iron rod is bored from both the ends and a very thin iron partition is left. One end of this tube is then made conical so as to fit exactly into the cone of the graphite tube. The tube is then bent into the shape as shown in figure (1), so that the molten salt may not run down the graphite tube. The thermocouple T is placed on the other side of the diaphragm as shown in the figure. Over the iron tube some mica is put and then the furnace is made by winding nichrome wire on it. The cone C is pushed inside the graphite tube, into a temperature region which is greater than the temperature at which the salt vaporises. This ensures that the salt vapour does not condense between the furnace and the high temperature region.
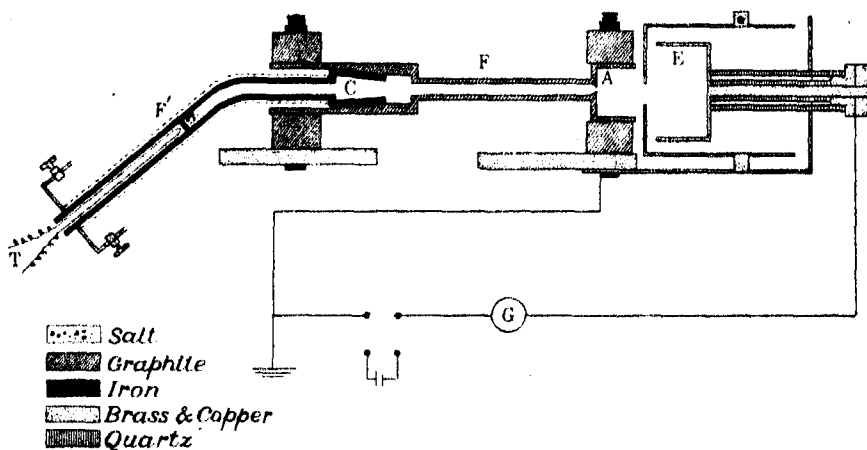
Fig. 1.

The salt to be investigated is put inside this furnace and the temperature is measured by means of a thermocouple.

At a distance d from the small hole in the graphite is put a diaphragm D of radius r, behind which is placed a Faraday cylinder E. The cylinder is connected to a sensitive galvanometer. If S denotes the area of the circular orifice, the number of particles coming out of the hole per second is given by $\frac{S}{4} n\bar{c}$, where n is the number of particles per cubic centimeter inside the graphite tube and $\bar{c}$ the mean velocity at the temperature of the graphite tube.

Now the pressure $p = nkT$ or $n = p/kT$ where p is the pressure of the particles inside the tube.

If p_{M^+} be the partial pressure of the positive ions inside the tube, then the number of positive particles coming out per second is equal to $\frac{S}{4}\frac{p}{kT}\bar{c}$ and therefore the positive ion current i_{M^+} is given by

$$i_{M^+} = \frac{S}{4}\frac{p_{M^+}}{kT} e \sqrt{\frac{8kT}{m\pi}}.$$

If i_g is the current indicated by the galvanometer

$$i_{M^+} = \frac{2d^2}{r^2} i_g$$

therefore

$$p_{M^+} = \frac{i_{M^+}}{eS} \sqrt{2\pi m_M kT}.$$

Similarly

$$p_{X^-} = \frac{i_{X^-}}{eS} \sqrt{2\pi m_M kT}.$$

If p_{MX} denotes the vapour pressure of the salt MX, then the dissociation constant K_2 is equal to $\dfrac{p_{M^+} \cdot p_{X^-}}{p_{MX}}$ and is therefore given by the expression

$$K_2 = \frac{i_{M^+} l_{X^-}}{e^2 S^2} \; (2\pi kT) \sqrt{\frac{m_M m_X}{p_{MX}}}.$$

The magnitude of the currents is measured experimentally by the galvano-meter. The diameter of the effusion hole is determined by means of a travelling microscope, from which S is calculated.

Experimental technique.—It is first of all necessary to study the emissions from the graphite tube when no salt is put inside the subsidiary furnace. For this reason the furnace tube is heated for an hour at a temperature of about 2000°C. in a vacuum of about 10^{-4} mms. The process is continued till the vacuum remains undisturbed by the heating of the graphite tube.

The Faraday cylinder is then given a small positive or negative voltage with respect to the graphite tube from a potential divider and the current due to electrons and positive ions is measured at different temperatures with different applied voltages. The positive current is found to be negligible in comparison to the negative current, which must be due to electrons emitted from the graphite tube.

The furnace is then opened and the salt is introduced into the subsidiary furnace. After proper degassing of the graphite tube the current in the subsidiary furnace is switched on. The temperature takes a steady value in about 15 minutes. The currents due to the positive and negative ions is measured again in the manner described above by giving the Faraday cylinder a small negative or positive potential with respect to the graphite tube, which is always kept at earth potential. The retarding potential is usually kept two volts but in the case of lithium chloride, the order of the electron current is comparable with the current due to the chlorine ions and so while measuring the chlorine ion current the retarding potential is kept very low. If the potential is kept high the electrons are accelerated and an unusually high current is recorded.

The temperature of the graphite tube is recorded by means of a disappearing filament type of pyrometer having two ranges. A nickel nichrome thermo-couple is used to indicate the temperature at which the salt vaporises. It is very necessary that during the experiment the temperatures remain steady.

There is no difficulty in maintaining steadiness of temperature in the case of the subsidiary furnace, but the temperature of the graphite tube sometimes fluctuates by small amounts due to the fluctuations in the voltage of the supply mains. For this reason, it becomes necessary to record the temperature of the graphite tube at very short intervals.

The experiments have been performed with three salts, KCl, NaCl and LiCl. The results obtained with each salt are given below and discussed separately.

Potassium Chloride.

The heat of ionisation of potassium is well known to be 99·5 Kilo calories. The heat of dissociation of potassium chloride into a potassium and chlorine atom is known to be 101·4 Kcal. The order of ion currents obtained in this case is of much greater order than the electron current (obtained from a blank experiment) and therefore the presence of the latter does not disturb the equilibrium represented by equation (2). Theoretically the positive ion current and the current due to chlorine ions should vary inversely as the square root of their atomic weights, and the effect of the extra electrons due to the graphite should increase the proportion of chlorine ions, but on the contrary it was found in many cases that the positive ion current was slightly larger than the chlorine ion current at low temperatures. This is probably due to the formation of molecular chlorine, according to equation (5), which diminishes the pressure of chlorine atoms, and hence the chlorine ion concentration decreases according to the equation (4). At higher temperatures the formation of molecular chlorine diminishes and more electrons are given out by the graphite tube, hence the current due to the chlorine ions increases in proportion. Table 1 gives the results of observations. The vapour pressure of KCl was directly extrapolated from the empirical formula of Fiöch and Rodebush [12].

$$\log p_{mm} = -\frac{9115}{T} + 8·3526$$

<div align="center">TABLE 1.</div>

Diameter of the effusion hole. (mms.).	Vapour pressure (dynes/cm²).	Temperature of the graphite tube. (°C.)	$i_{K^+} \times 10^6$ (amps.)	$i_{Cl^-} \times 10^6$ (amps.)	$K \times 10^5$	Q (Kilo cals.)
1·17	90·95	1620	583·4	583·4	127·6	114·7
„	84·48	1560	37·04	34·61	52·72	114
„	27·66	1530	24·5	21·78	41·6	113·6
„	15·2	1380	4·668	4·279	3·909	111
·4955	28·3 ✳	1625	11·97	17·96	114	114·8
„	15·55	1625	16·16	15·19	276·2	112
„	17·33	1550	8·079	5·171	40·51	114·2
„	111·1	1540	25·22	12·93	49·03	112·9
„	17·33	1520	5·819	3·555	19·72	114·8

Taking the mean of the above values of Q we get 113·5 Kilo calories, and hence from the formula $E = D + I - Q$ we get $\{99\cdot5 + 101\cdot4 - 113\cdot5\} = 87\cdot4$ Kilo calories for the value of the electron affinity of chlorine.

Sodium Chloride.

The results obtained with sodium chloride vapour are given in table 2. It will be found that the positive ion current is much larger than the current due to the negatively charged chlorine ions, specially at low temperatures and pressures. The atomic weight of sodium (23) is smaller than that of chlorine (35·5) and so the effusion current due to Na^+ should be larger by 1·243 times, but it will be seen that the current is sometimes twice or even more. The cause is again due to the formation of molecular chlorine as explained in the case of potassium chloride. At high temperatures the proportion of chlorine ions increases. The vapour pressure of sodium chloride has been calculated from the empirical formula of Fiöch and Rodebush [12].

$$\log_{10} p_{mm} = -\frac{9419}{T} + 8\cdot3297$$

TABLE 2.

Diameter of the effusion hole.	Vapour pressure (dynes/cm²).	Temperature of the graphite tube. (°C.)	$i_{Na^+} \times 10^7$ (amps.)	$i_{Cl^-} \times 10^7$ (amps.)	$K \times 10^7$	Q (Kilo cals.)
1·17 mm.	82·59	1625	70·87	57·57	128·5	132·4
,,	11·71	1620	27·52	25·6	180·3	131·7
,,	61·37	1600	103·7	64·82	283·2	127·7
,,	41·49	1560	74·54	45·37	206·3	126
,,	15·81	1505	21·34	5·762	19	130·5
,,	11·71	1500	14·41	5·403	16·26	130·7
,,	76·9	1470	30·4	14·99	14·24	128·7
,,	15·81	1450	11·89	3·60	6·439	130
,,	11·71	1450	7·565	2·881	4·422	131·3
,,	31·11	1440	10·87	4·478	3·701	131·1
,,	76·9	1400	21·07	9·317	5·895	126·3

The average of Q from the above comes out to be 129·7 Kilo calories. The heat of dissociation of sodium chloride into sodium and chlorine is known to be 97·7 Kilo calories and the ionisation potential of sodium is 117·9 Kilo calories. The electron affinity of chlorine is therefore $(97\cdot7 + 117\cdot9 - 129\cdot7) = 85\cdot9$ Kilo calories.

Lithium Chloride.

It has been seen in the ionisation of KCl and NaCl that the current due to chlorine ions is diminished due to the formation of molecular chlorine. It is therefore to be expected that in the case of lithium chloride the proportion of

chlorine ions would be much smaller. On the contrary it was found that the number of chlorine ions was much larger than the number of lithium ions. Lithium has a high ionisation potential of 123·8 Kilo calories and the heat of dissociation of LiCl is also very large (114·4 Kilo calories). The order of currents obtained at the temperatures used (1400°C.—1625) is therefore of much smaller magnitudes than the corresponding currents for KCl and NaCl. The electron current due to the emission from the graphite tube was negligible in the latter cases, but in this case it is of the same order as the current due to the ions. The effect of a large percentage of free electrons will naturally be to retard the ionisation of lithium and to accelerate the formation of chlorine ions. It is for this reason that chlorine ions are present in such a large proportion.

As no arrangement has yet been made to distinguish between the negative ion and electron currents, it has been supposed here the negative current is all due to the chlorine ions. This may introduce an error in this case. Attempt was made to carry out the experiments at low temperatures in the absence of free electrons but then the currents were so small that the galvanometer could not detect them. One extra precaution has however been taken in this case. The retarding potential, while measuring the chlorine ion current, was kept very low (0·5 volt) because of the presence of electrons. A large voltage accelerates the electrons and an unusually high current is obtained.

The results obtained are tabulated in table 3. The vapour pressure has been extrapolated from the formula given by Wartenburg and Schulz [13].

$$\log p_{atm} = -\frac{37200}{4 \cdot 57\ T} + 4 \cdot 923$$

TABLE 3.

Diameter of the effusion hole.	Vapour pressure (dynes/cm²).	Temperature of the graphite tube. (°C.)	$i_{Li^+} \times 10^8$ (amps.)	$i_{Cl^-} \times 10^8$ (amps.)	$K \times 10^{10}$	Q (Kilo cals.)
1·17 mm.	139	1660	98·54	262·8	2743	148·7
,,	360·6	1640	102·2	240·8	979·7	151·1
,,	139	1625	73	175·2	1330	148·8
,,	203·7	1620	43·8	153·3	475·2	152·4
,,	77·27	1610	37·35	79·41	550·9	150·9
,,	77·27	1575	32·79	42·05	250·4	150·9
,,	307·6	1420	9·344	9·344	3·659	152

CONCLUSION.

In this paper is described an experimental method for finding out the electron affinity of the halogens. The method has for the present been applied to chlorine only. The value of this quantity, from the two sets of most reliable

determinations, comes out to be 86·6 Kilo cals. and the theoretical value given by Born, Mayer and Helmholtz[1] is also 86·5. The results are therefore in perfect agreement with the theory. Further experiments are in progress for finding out, according to this method, the electron affinity of the other halogens.

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THE PROBLEM OF k SAMPLES FOR POISSON POPULATION.

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INTRODUCTION.

A good many contributions have been added in recent years to the 'Problem of k Samples' as formulated by Neyman and Pearson. The discussion is confined to Normal Law Variation and little or no attention is paid to non-normal populations. The first attempt in this direction was probably that of the author (1) who considered the case of Exponential Law Variation and developed a technique of analysis completely analogous to that of Neyman and Pearson. The object of this paper is to consider the problem in relation to yet another two populations—the Poisson and the Binomial Series—the technique for which is fairly known in the works of Fisher. The main interest of the paper, however, is that the technique of this paper forms an alternative approach to the 'Interval' technique of analysis discussed by the author (1).

THE HYPOTHESES CONSIDERED.

It is known that if an event occurs randomly in space or time and the variable considered is the number of occurrences counted in a fixed space or time interval, then the chances that this variable takes values $0, 1, \ldots x \ldots$ are given by the terms of the Poisson series

$$e^{-m}\left(1, m, m^2, \ldots \ldots \frac{m^x}{x!} \ldots \right).$$

Suppose we have a type of data arranged as follows :—

$$
\begin{array}{lllll}
x_{11} & x_{21}\ldots\ldots x_{t1}\ldots x_{k1} \\
x_{12} & x_{22}\ldots\ldots x_{t2}\ldots x_{k2} \\
\vdots & \vdots \quad\quad \vdots \quad\quad \vdots \\
x_{1n}\ldots x_{2n}\ldots\ldots x_{tn}\ldots x_{kn}
\end{array} \quad\quad .. \quad\quad .. \quad\quad .. \quad (1)
$$

where x_{ti} is the number of occurrences counted in a fixed time or space interval and the chance that the variable in the tth column and the ith row takes the value x_{ti} given by

$$e^{-m_{ti}} \frac{(m_{ti})^{x_{ti}}}{x_{ti}!} \quad\quad .. \quad\quad .. \quad\quad .. \quad\quad .. \quad (2)$$

Thus in the case of the telephone problem considered in my paper (1), if n represents the number of time units during the day and k the number of

stations, then x_{ti} will be the number of calls arrived during the ith unit at the tth exchange. The problems for consideration would then be whether

   (a) the intensity of traffic during the day (or part of the day) varies more than might be expected through chance causes ;

   (b) the traffic is significantly different at different exchanges, assuming that during the day its intensity is the same at every station ;

   (c) the whole set of record (or part of the set within a rectangle) could be combined together without loss of homogeneity.

Analytically these problems would take the following form :—

   (a) The hypothesis H_1 that the variation within columns is no more than might be expected through chance causes. That is to say

$$m_{t1} = m_{t2} = \ldots\ldots = m_{tn} \quad (t = 1, \ldots k) \ldots \qquad .. \qquad .. \qquad (3)$$

   (b) The hypothesis H_2. Here it is assumed that

$$m_{t1} = m_{t2} = \ldots\ldots = m_{tn} = m_t \text{ say}$$

the hypothesis to be tested is then that

$$m_1 = m_2 = \ldots\ldots = m_t = \ldots = m_k \qquad .. \qquad .. \qquad .. \qquad (4)$$

   (c) The hypothesis H that the whole set of observations have come from some common Poisson population. That is to say whether (3) and (4) are true.

Our purpose is to determine from the observed data suitable criteria to test the hypotheses H_1, H_2 and H, and to obtain their sampling distributions. The likelihood ratio as defined by Neyman and Pearson (2, 3) has proved to be a very powerful method in determining suitable tests of the statistical hypotheses. In the case of Normal Law Variation the method leads to the usual analysis of variance tests and to certain new tests of practical value. In the case of the χ^2 law variation with two degrees of freedom the method has again proved to be of immense use. We shall use the same in the present instance and shall find that the method leads to the well-known χ^2 tests first given by R. A. Fisher (4).

THE DERIVATION OF CRITERIA.

The probability function for the joint occurrence of the nk values is obtained by multiplying expressions of the type (2) and may therefore be written

$$p = e^{-S(m_{ti})} \prod_{t=1}^{k} \prod_{i=1}^{n} \frac{(m_{ti})^{x_{ti}}}{x_{ti}!} \qquad .. \qquad .. \qquad .. \qquad (5)$$

The method of likelihood ratio consists in defining two sets of conditions : (a) the conditions which are assumed to be satisfied ; (b) the conditions which define the hypothesis to be tested. Thus considering the hypothesis H_1, the conditions (a) are that the observations x_{ti} have been drawn from the same Poisson population m_{ti} and the conditions (b) are that same

$$m_{t1} = m_{t2} = \ldots\ldots = m_{tn} = m_t \text{ say} ;$$

so that the observations in the tth group are drawn from a common Poisson population $m_t(t = 1, \ldots k)$. The conditions (a) define a class Ω of admissible set of populations m_{ti} and the conditions (b) define a sub-class ω, of Ω to which m_{ti} must belong if the hypothesis tested be true.

The maximum value of p in equation (5) associated with Ω is called $p(\Omega \text{ max.})$ and associated with ω is called $p(\omega \text{ max.})$. The likelihood ratio is then defined as

$$\lambda = \frac{p(\omega \text{ max.})}{p(\Omega \text{ max.})} \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (6)$$

which is supposed to give the suitable criterion of the hypothesis. For it is clear that λ must vary between 0 and 1 and that the smaller the value of λ the less likely is it that the populations belong to ω, that is that the hypothesis tested is true.

Consider the hypothesis H_1.

The conditions (a) and (b) are already defined above. The set Ω consists of populations $m_{ti}(t = 1, \ldots, k; i = 1, \ldots n)$ and the subset ω consists of populations $m_t(t = 1, \ldots k)$ to which the tth group $(t = 1, \ldots k)$ belongs.

We have from the relation (5)

$$\log p = -S(m_{ti}) + S\{x_{ti} \log m_{ti}\} - S\{\log x_{ti}!\}$$

$$\therefore \quad \frac{\partial \log p}{\partial m_{ti}} = -1 + \frac{x_{ti}}{m_{ti}}$$

whence for the maximum value of p, we have

$$m_{ti} = x_{ti}$$

giving us

$$p(\Omega \text{ max.}) = e^{-S(x_{ti})} \prod_{t=1}^{k} \prod_{i=1}^{n} \frac{(x_{ti})^{x_{ti}}}{x_{ti}!} \cdots \quad \cdots \quad \cdots \quad (7)$$

In exactly the same way we have for the subset ω

$$\log p = -S(m_t) + S(x_{ti} \log m_t) - S\{\log x_{ti}!\}$$

giving us

$$\frac{\partial \log p}{\partial m_t} = -n + \frac{S(x_{ti})}{m_t}$$

where the summation S extends over the values in the tth group.

For the maximum value of p we have

$$m_t = \bar{x}_t \cdot = \frac{S(x_{ti})}{n}$$

and

$$p(\omega \text{ max.}) = e^{-S(\bar{x}_t)} \prod_{t=1}^{k} \prod_{i=1}^{n} \frac{(\bar{x}_t)^{x_{ti}}}{x_{ti}!} \quad \cdots \quad \cdots \quad (8)$$

Hence

$$\lambda_{H_1} = \frac{p(\omega \text{ max.})}{p(\Omega \text{ max.})} = \frac{\prod\limits_{t=1}^{k} (\bar{x}_{t\cdot})^{n\bar{x}_{t\cdot}}}{\prod\limits_{t=1}^{k} \prod\limits_{i=1}^{n} (x_{ti})^{x_{ti}}} \qquad .. \qquad .. \qquad (9)$$

Following the same procedure we shall have

$$\lambda_{H_2} = \prod\limits_{t=1}^{k} \left(\frac{\bar{x}_{\cdot\cdot}}{\bar{x}_{t\cdot}}\right)^{n\bar{x}_{t\cdot}} \qquad .. \qquad .. \qquad .. \qquad (10)$$

where $\bar{x}_{\cdot\cdot}$ denotes the mean of the whole set of N observations and

$$\lambda_H = \frac{(\bar{x}_{\cdot\cdot})^{N\bar{x}_{\cdot\cdot}}}{\prod\limits_{t=1}^{k} \prod\limits_{i=1}^{n} (x_{ti})^{x_{ti}}} \qquad .. \qquad .. \qquad .. \qquad (11)$$

where $N = nk$.

It will be noticed that

$$\lambda_H = \lambda_{H_1} \times \lambda_{H_2} \qquad .. \qquad .. \qquad .. \qquad (12)$$

If λ is to be regarded as the fundamental criterion of the hypothesis, we shall have to obtain the probability $P\{\lambda \leqslant \lambda_0\}$ that λ is less than or equal to a given value λ_0 if the hypothesis tested be true. It will be found, however, that the approach to this problem necessarily involves limiting approximations, one of these being the approximate expression for λ itself. These approximate expressions for λ's are found identical with Fisher's indices of dispersion. Thus for λ_H we have

$$-\log \lambda_H = S\{x_{ti} (\log x_{ti} - \log \bar{x})_{\cdot\cdot}\} \qquad .. \qquad .. \qquad (13)$$

Substituting

$$x_{ti} = \bar{x}_{\cdot\cdot} + z_{ti}\sqrt{\bar{x}_{\cdot\cdot}} \qquad .. \qquad .. \qquad .. \qquad (14)$$

$$-\log \lambda_H = S(\bar{x}_{\cdot\cdot} + z_{ti}\sqrt{\bar{x}_{\cdot\cdot}}) \left\{\log \left(1 + \frac{z_{ti}}{\sqrt{\bar{x}_{\cdot\cdot}}}\right)\right\}^{*}$$

$$= \frac{1}{2} S(z^2_{ti}) - \frac{1}{2} \frac{1}{\sqrt{\bar{x}_{\cdot\cdot}}} S(z^3_{ti})$$

$$+ \frac{1}{3} \frac{1}{\sqrt{\bar{x}_{\cdot\cdot}}} S \frac{z^3_{ti}}{\left(1 + \theta \frac{z_{ti}}{\sqrt{\bar{x}_{\cdot\cdot}}}\right)^{3}} + \frac{1}{3} \frac{1}{\bar{x}_{\cdot\cdot}} S \left\{\frac{z^4_{ti}}{\left(1 + \theta \frac{z_{ti}}{\sqrt{\bar{x}_{\cdot\cdot}}}\right)^{3}}\right\}$$

$$0 < \theta < 1$$

$$= \frac{1}{2} S(z^2_{ti}) + \eta \qquad .. \qquad .. \qquad .. \qquad .. \qquad (15)$$

---

* The expansion of $\log \left(1 + \frac{z}{a}\right)$ is valid if z/a is less than one. This may not, however, always happen. But it may be shown that within the boundary of the Best Critical Region its value is less than one and that the expansion is valid.

where η can be made as small as possible by making $\bar{x}_{..}$ sufficiently large, which is a direct consequence of the fact that m is large.

We thus have the result that the distribution of $-2 \log \lambda_H$ approximates to that of $\dfrac{S(x_{ti}-\bar{x}_{..})^2}{\bar{x}_{..}}$ as m becomes large.

In the same way we shall have

$$-2 \log \lambda_{H_1} = S\left\{ \frac{(x_{ti}-\bar{x}_{t.})^2}{\bar{x}_{t.}} \right\} \qquad .. \qquad .. \qquad .. \quad (16)$$

and

$$-2 \log \lambda_{H_2} = S\left\{ \frac{(\bar{x}_{t.}-\bar{x}_{..})^2}{\bar{x}_{..}} \right\} \qquad .. \qquad .. \qquad .. \quad (17)$$

THE DISTRIBUTIONS.

The expressions on the right hand side of equations (15), (16) and (17) resemble the ordinary χ^2 and are known to be distributed in a Pearsonian χ^2 distribution with $kn-1$, $k(n-1)$ and $k-1$ degrees of freedom. A rigorous proof giving the distribution of χ^2 may be made in more than one way. It is proposed in this paper to follow the method of Kolodziejczyk (5) who gave the proof for the distribution of χ^2 for a single sample of the Binomial series, and show that the χ^2 for samples of the Poisson series follows with good approximation the Pearsonian distribution for large value of m.

It is clear that we need consider the distribution of only one of the three forms of χ^2 given above—say the first. Denote by $P\{\chi^2 \leqslant \chi^2{}_0\}$ the probability that χ^2 is less than say $\chi^2{}_0$. It follows :—

$$P\{\chi^2 \leqslant \chi^2{}_0\} = S\left\{ \prod_{t=1}^{k} \prod_{i=1}^{n} e^{-m}\frac{m^{x_{ti}}}{x_{ti}!} \right\} \qquad .. \qquad .. \quad (18)$$

where the summation S extends over the system of values given by

$$\chi^2 = \frac{S(x_{ti}-\bar{x}_{..})^2}{\bar{x}_{..}} \leqslant \chi^2{}_0 \qquad .. \qquad .. \qquad .. \quad (19)$$

Since it may be shown that the sum of a given number of terms of the Poisson series can be represented with good approximation by the integral of a normal curve with the same mean and standard deviation when m is large, we may for large values of m write

$$P\{\chi^2 \leqslant \chi^2{}_0\} = \frac{1}{(\sqrt{2\pi m})^N}\int_{W_0}\ldots\int e^{-\frac{S(x_{ti}-m)^2}{2m}} \prod_{t=1}^{k} \prod_{i=1}^{n} dx_{ti}+\eta \quad .. \quad (20)$$

where x_{ti} are assumed continuous, W_0 denotes the region defined in (19) and η can be made as small as possible by making m sufficiently large. That is to say, given ϵ, any $+ve$ number, however small, we can always find a number m_0 such that for $m > m_0$, $|\eta| < \epsilon$.

Let us put

$$\frac{1}{(\sqrt{2\pi m})^N} \int_{W_0} \cdots \int e^{-\frac{S(x_{ti}-m)^2}{2m}} \prod_{t=1}^{k} \prod_{i=1}^{n} dx_{ti} = I(W_0) \quad \cdots \qquad \cdots \quad (21)$$

and choose a positive number Q such that

$$I(W_1) = \left(\frac{1}{\sqrt{2\pi}}\right)^N \int_{W_1} \cdots \int e^{-\frac{S(y^2_{ti})}{2}} \prod_{t=1}^{k} \prod_{i=1}^{n} dy_{ti} > 1 - \epsilon \qquad \cdots \quad (22)$$

where W_1 is defined by

$$\frac{S(x_{ti}-m)^2}{m} \leqslant Q^2 \quad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \quad (23)$$

and

$$y_{ti} = \frac{x_{ti}-m}{\sqrt{m}} \qquad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \quad (24)$$

Consider the region W_2—the part common to W_0 and W_1. It follows that

$$P\{\chi^2 \leqslant \chi^2_0\} = I(W_2) + \eta_2 \qquad \cdots \qquad \cdots \qquad \cdots \quad (25)$$

where

$$|\eta_2| < 2\epsilon \quad \text{for } m \geqslant m_0.$$

It should be noted that for all points in the region W_2 we have

$$|x_{ti}-m| < Q\sqrt{m} \cdots \qquad \cdots \qquad \cdots \qquad \cdots \quad (26)$$

$$\therefore \ |\bar{x}-m| < Q\sqrt{m} \cdots \qquad \cdots \qquad \cdots \qquad \cdots \quad (27)$$

and hence

$$|x_{ti}-\bar{x}| < 2Q\sqrt{m} \qquad \cdots \qquad \cdots \qquad \cdots \quad (28)$$

Consider the regions W_3 and W_4 defined by

$$\left. \begin{array}{c} \dfrac{S(x_{ti}-\bar{x})^2}{\bar{x}} < \chi^2_0 - \epsilon \\[2mm] \dfrac{S(x_{ti}-m)^2}{m} < Q^2 \end{array} \right\} \qquad \cdots \qquad \cdots \qquad \cdots \quad \begin{array}{c} (29) \\[4mm] (30) \end{array}$$

and

$$\left. \begin{array}{c} \dfrac{S(x_{ti}-\bar{x})^2}{\bar{x}} < \chi^2_0 + \epsilon \\[2mm] \dfrac{S(x_{ti}-m)^2}{m} < Q^2 \end{array} \right\} \qquad \cdots \qquad \cdots \qquad \cdots \quad \begin{array}{c} (31) \\[4mm] (32) \end{array}$$

It follows that

$$W_3 < W_2 < W_4 \quad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \quad (33)$$

where the symbol $<$ denotes ' contained in ' and

$$I(W_3) < I(W_2) < I(W_4) \qquad \cdots \qquad \cdots \qquad \cdots \quad (34)$$

Now the inequalities (29) and (31) may be written as

$$\frac{S(x_{ti}-\bar{x}_{..})^2}{m} \leqslant (\chi^2_0 - \epsilon)\left(1 + \frac{\bar{x}_{..}-m}{m}\right) \qquad .. \qquad .. \quad (35)$$

and

$$\frac{S(x_{ti}-\bar{x}_{..})^2}{m} < (\chi^2_0 + \epsilon)\left(1 + \frac{\bar{x}_{..}-m}{m}\right) \qquad .. \qquad .. \quad (36)$$

whence it is clear that by increasing m if necessary we shall have

$$\chi^2_0 > (\chi^2_0 - \epsilon)\left(1 + \frac{\bar{x}_{..}-m}{m}\right) > \chi^2_0 - 2\epsilon \qquad .. \qquad .. \quad (37)$$

and

$$\chi^2_0 < (\chi^2_0 + \epsilon)\left(1 + \frac{\bar{x}_{..}-m}{m}\right) < \chi^2_0 + 2\epsilon. \qquad .. \qquad .. \quad (38)$$

Denote by W_5 and W_6 the regions defined by

$$\frac{S(x_{ti}-\bar{x}_{..})^2}{m} \leqslant \chi^2_0 - 2\epsilon \left.\vphantom{\frac{S(x_{ti}-m)^2}{m}}\right\} \qquad .. \qquad .. \qquad .. \quad (39)$$

$$\frac{S(x_{ti}-m)^2}{m} \leqslant Q^2 \qquad .. \qquad .. \qquad .. \quad (40)$$

and

$$\frac{S(x_{ti}-\bar{x}_{..})^2}{m} \leqslant \chi^2_0 + 2\epsilon \left.\vphantom{\frac{S(x_{ti}-m)^2}{m}}\right\} \qquad .. \qquad .. \qquad .. \quad (41)$$

$$\frac{S(x_{ti}-m)^2}{m} \leqslant Q^2 \qquad .. \qquad .. \qquad .. \quad (42)$$

We then have for m sufficiently large

$$W_5 < W_3 < W_2 < W_4 < W_6 \qquad .. \qquad .. \qquad .. \quad (43)$$

giving us the result

$$I(W_5) \leqslant I(W_2) \leqslant I(W_6) \qquad .. \qquad .. \qquad .. \quad (44)$$

Consider now the regions W_7 and W_8 corresponding to the inequalities (39) and (41) respectively. Then owing to the property of the number Q, we have for $m > m_0$

$$I(W_7) = I(W_5) + \eta_4 \qquad .. \qquad .. \qquad .. \qquad .. \quad (45)$$

and

$$I(W_8) = I(W_6) + \eta_5 \qquad .. \qquad .. \qquad .. \qquad .. \quad (46)$$

where

$$|\eta_4| \text{ and } |\eta_5| \text{ are each less than } \epsilon.$$

But the probability integral of $\frac{S(x_{ti}-\bar{x}_{..})^2}{m}$ is the well-known ordinary χ^2 integral, whence we have

$$\lim_{m \to \infty} P\{\chi^2 > \chi^2_0\} = (2)^{\frac{1}{2}f}\Gamma(\tfrac{1}{2}f)\int_{\chi^2_0}^{\infty}(\chi^2)^{\frac{1}{2}f-1}e^{-\frac{1}{2}\chi^2}d(\chi^2) \quad .. \qquad ,. \quad (47)$$

where f = number of degrees of freedom

$= N - 1$.

In exactly the same way it may be shown that the two forms of χ^2 for H_1 and H_2 hypotheses follow χ^2-distribution with degrees of freedom equal to $k(n-1)$ and $k-1$ respectively.

THE BINOMIAL SERIES.

Analogous procedure may be followed in the case of Binomial series. The data such as those on page 297 may now arise in a variety of ways. Thus for example, the n values of x in the tth column may represent the number of infested barley ears in n samples of, say, 20 each, drawn from the ith plot and k will represent the number of plots and the problems for consideration would then be whether the material is homogeneous within a plot, whether the proportion of infestation varies considerably from plot to plot and so on.

The complete form of χ^2-technique is given in Table I where in the case of the Binomial series

p_t . represents the proportion of infested ears on the tth plot ;

$p_{..}$ is the proportion of infested ears on all the plots ;

$q_t . = 1 - p_t .$ and $q_{..} = 1 - p_{..}$.

and the notation used for the Poisson series is one that has been already explained.

<div align="center">TABLE I.</div>

Variation.	λ-criteria for Poisson Series.	χ^2 Poisson Series.	χ^2 Binomial Series.	Degrees of freedom.
Within Columns ..	$\dfrac{\prod\limits_{t=1}^{k} (\bar{x}_t .)^{n\bar{x}_t .}}{\prod\limits_{t=1}^{k}\prod\limits_{i=1}^{n} (x_{ti})^{x_{ti}}}$	$S\left\{ \dfrac{(x_{ti} - \bar{x}_t .)^2}{\bar{x}_t .} \right\}$	$S\left\{ \dfrac{(x_{ti} - \bar{x}_t .)^2}{\bar{x}_t . q_t .} \right\}$	$k(n-1)$
Between Columns ..	$\prod\limits_{t=1}^{k} \left(\dfrac{\bar{x}_{..}}{\bar{x}_t .} \right)^{n\bar{x}_t}$	$S\left\{ \dfrac{(\bar{x}_t . - \bar{x}_{..})^2}{\bar{x}_{..}} \right\}$	$S\left\{ \dfrac{(\bar{x}_t . - \bar{x}_{..})^2}{\bar{x}_{..} q_{..}} \right\}$	$k-1$
Total	$\dfrac{(\bar{x}_{..})^{N\bar{x}_{..}}}{\prod\limits_{t=1}^{k}\prod\limits_{i=1}^{n} (x_{ti})^{x_{ti}}}$	$\dfrac{S(x_{ti} - \bar{x}_{..})^2}{\bar{x}_{..}}$	$\dfrac{S(x_{ti} - \bar{x}_{..})^2}{\bar{x}_{..} q_{..}}$	$kn-1$

In conclusion it must be emphasized that the expressions obtained for the probability $P\{\chi^2 \leqslant \chi^2_0\}$ are only approximate and hold true in the limit when m is sufficiently large. The effect of this stipulation in practice and the illustration of the uses of these tests are discussed elsewhere (6). It is found

that when m is as large or larger than 3, the χ^2-forms for the Poisson series follow the ordinary χ^2-distribution with good approximation and that the χ^2-tables may be used with confidence (7).

SUMMARY.

A statistical technique called the technique of 'Count' analysis for samples drawn at random from a Poisson population has been developed. In particular three statistical hypotheses corresponding to Neyman and Pearson's H_1, H_2 and H hypotheses for Normal Law Variation are considered and the principle of likelihood ratio is applied to get suitable criteria based on observations. It is shown that the criteria follow the well-known Pearsonian χ^2-distribution with degrees of freedom appropriate to respective hypotheses. It is emphasized that the tests are approximate and that the approximation becomes satisfactory when m, the population parameter, is as large or larger than 3. A similar set of hypotheses with their criteria are given for samples of the Binomial series.

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REFLECTIONS FROM THE IONOSPHERE.

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A large amount of work [1] has been done on the study of the propagation
of wireless waves through the ionosphere. Mary Taylor [2] has drawn dispersion
curves for the general Appleton-Hartree formula taking different values of
the friction and Booker [3] has attempted a general theoretical investigation
of the state of polarisation, absorption and the condition of reflection of the
waves. In all these discussions it has been supposed that the condition of
reflection of the waves from the ionosphere is obtained by equating the real
part of the complex refractive index to zero. While for oblique propagation,
it is physically quite plausible that there will be total reflection of the waves
when the value of μ falls below a critical value depending upon the initial
angle of incidence, it is not quite clear why the waves should be reflected in
the case of vertical propagation when the value of μ is nearly zero. It is more
correct to say that reflection takes place when the group velocity vanishes.

Though this suggestion was first made by Appleton [4] in 1928 it appears
that nobody has so far taken serious notice of this suggestion. In fact, every-
body seems to have assumed that we have, in all cases

$$UV = c^2 \qquad .. \qquad .. \qquad .. \qquad .. \qquad (1)$$

But it can be shown that this relation holds only in the absence of the
magnetic field.

Thus Prof. S. K. Mitra in his well-known report[1] says, on p. 164, that $U = c\mu$
in cases where the action of the earth's magnetic field can be neglected, i.e.
for short waves. But it will be presently shown that even in this case, the
relation is not correct when the electron-density is sufficiently large. Further,
Booker [3] has assumed that in the general case ($H \neq 0$) the group path is given
by

$$P' = \int \frac{ds}{\mu} \qquad .. \qquad .. \qquad .. \qquad .. \qquad (2)$$

So here clearly the assumption is made that the group velocity $U = c\mu$ even
when $H \neq 0$.

GROUP VELOCITY IN THE IONOSPHERE.

To simplify the mathematical working we have taken friction to be zero
although small values of collisional frequency will not appreciably alter the
results.

The group velocity U is given by the formula

$$\frac{1}{U} = \frac{dk}{d\nu} = \frac{d}{d\nu}\left(\frac{\nu}{V}\right) \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where ν is the frequency, k the wave number and V the phase velocity of the waves. This formula was originally proved by Lord Rayleigh [5] for a frictionless medium, but nobody seems to have worked out how the formula will be modified when absorption is considerable. Since $V = \dfrac{c}{\mu}$, where c is the velocity of light in vacuo,

$$\frac{1}{U} = \frac{1}{c}\frac{d}{d\nu}(\mu\nu) = \frac{1}{c}\frac{d}{dp}(\mu p) \quad .. \quad .. \quad .. \quad (4)$$

where $p = 2\pi\nu$. The above can be written, if we put $\mu^2 = \delta$, as

$$\frac{1}{U} = \frac{\delta^{1/2}}{c}\left[1 + \frac{1}{2}\frac{p}{\delta}\cdot\frac{d\delta}{dp}\right] = \frac{\delta^{1/2}}{c}\left[1 + \frac{p}{2}\frac{d}{dp}(ln\delta)\right] \quad .. \quad (5)$$

Now we have

$$\delta = \mu^2 = 1 + \frac{1}{X},$$

where

$$X = -\frac{1}{x}\left[1 - \frac{y_T^2/2}{1-x} \pm \sqrt{y_L^2 + \frac{y_T^4}{4(1-x)^2}}\right]$$

$$x = \frac{p_0^2}{p^2} \quad y_{L,T} = \frac{p_{L,T}}{p} \quad p_0 = \frac{4\pi Ne^2}{m} \quad p_{L,T} = \frac{eH_{L,T}}{mc}$$

e = the charge of the electron in e.s.u.

M = mass of the electron.

N = the electron density.

H_L = component of the magnetic field along the direction of propagation of the waves.

H_T = component of the magnetic field at right angles to the direction of propagation.

Putting these values of x, y_L and y_T, it can be easily shown that

$$\delta = \mu^2 = \frac{(p/p_0 - p_0/p)^2 - \dfrac{p^2}{2p_0} \pm \sqrt{\left(\dfrac{p}{p_0} - \dfrac{p_0}{p}\right)^2 \dfrac{p_L^2}{p_0^2} - \dfrac{p_1^4}{4p_0^4}}}{p^2/p_0^2 - 1 - \dfrac{p_T^2}{2p_0} \pm \sqrt{\left(\dfrac{p}{p_0} - \dfrac{p_0}{p}\right)^2 \dfrac{p_L^2}{p_0^2} + \dfrac{p_T^4}{4p_0^4}}}$$

$$= \frac{\left(w - \dfrac{1}{w}\right)^2 - A + \xi}{w^2 - 1 - A + \xi} \quad .. \quad .. \quad .. \quad (6)$$

where

$$\xi = \pm\sqrt{\left(w - \frac{1}{w}\right)^2 B + A^2} \quad .. \quad .. \quad .. \quad (7)$$

$$w = p/p_0 \qquad B = p_L^2/p_0^2 \qquad A = p_T^2/2p_0.$$

Now,

$$p \frac{d}{dp} (ln\delta) = p \frac{d}{dw} (ln\delta) \frac{dw}{dp} = w \frac{d}{dw} (ln\delta).$$

We therefore obtain

$$\frac{1}{U} = \frac{\delta^{1/2}}{c} \left[1 + \frac{w}{2} \frac{d}{dw} (ln\delta) \right] \qquad .. \qquad .. \qquad .. \quad (5')$$

Now,

$$ln\delta = ln \left[\left(w - \frac{1}{w} \right)^2 - A + \xi \right] - ln(w^2 - 1 - A + \xi)$$

and

$$\frac{d}{dw} (ln\delta) = \frac{2 \left(w - \frac{1}{w} \right) \left(1 + \frac{1}{w^2} \right) + \frac{d\xi}{dw}}{\left(w - \frac{1}{w} \right)^2 - A + \xi} - \frac{2w + \frac{d\xi}{dw}}{w^2 - 1 - A + \xi}$$

$$= \frac{2w \left[1 - \frac{2}{w^2} + \frac{1}{w^4} + \frac{A}{w^4} - \frac{\xi}{w^4} \right]}{\left[\left(w - \frac{1}{w} \right)^2 - A + \xi \right] [w^2 - 1 - A + \xi]}$$

$$+ \frac{d\xi}{dw} \frac{1 - \frac{1}{w^2}}{\left[\left(w - \frac{1}{w} \right)^2 - A + \xi \right] [w^2 - 1 - A + \xi]}.$$

Since

$$\xi = \pm \left\{ \left(w - \frac{1}{w} \right)^2 B + A^2 \right\}^{1/2}$$

$$\frac{d\xi}{dw} = \pm \frac{B \left(w - \frac{1}{w} \right) \left(1 + \frac{1}{w^2} \right)}{\left\{ \left(w - \frac{1}{w} \right)^2 B + A^2 \right\}^{1/2}}$$

$$= \frac{B \left(w - \frac{1}{w} \right) \left(1 + \frac{1}{w^2} \right)}{\xi}.$$

Hence,

$$\frac{1}{U} = \frac{\delta^{1/2}}{c} \left[1 + \frac{w}{2} \frac{d}{dw} (ln\delta) \right].$$

$$= \frac{\delta^{1/2}}{c} \left[1 + \frac{\left(w - \frac{1}{w} \right)^2 + \frac{A}{w^2} - \frac{\xi}{w^2} + \frac{B \left(w - \frac{1}{w} \right)^2 \left(1 + \frac{1}{w^2} \right)}{2\xi}}{\left[\left(w - \frac{1}{w} \right)^2 - A + \xi \right] [w^2 - 1 - A + \xi]} \right]$$

or

$$\frac{1}{U} = \frac{\delta^{1/2}}{c} \left[\frac{(w^2 - 1 - A + \xi)\left\{\left(w - \frac{1}{w}\right)^2 - A + \xi\right\} + \left(w - \frac{1}{w}\right)^2 + \frac{A}{w^2} - \frac{\xi}{w^2} + \dfrac{B\left(w - \frac{1}{w}\right)^2\left(1 + \frac{1}{w^2}\right)}{2\xi}}{(w - 1 - A + \xi)\left\{\left(w - \frac{1}{w}\right)^2 - A + \xi\right\}} \right]$$

$$= \frac{1}{c} \left[\frac{(w^2 - 1 - A + \xi)\left\{\left(w - \frac{1}{w}\right)^2 - A + \xi\right\} + \left(w - \frac{1}{w}\right)^2 + \frac{A}{w^2} - \frac{\xi}{w^2} + \dfrac{B\left(w - \frac{1}{w}\right)^2\left(1 + \frac{1}{w^2}\right)}{2\xi}}{(w^2 - 1 - A + \xi)^{3/2}\left\{\left(w - \frac{1}{w}\right)^2 - A + \xi\right\}^{1/2}} \right]$$

$$\frac{U}{c} = \frac{(w^2 - 1 - A + \xi)^{3/2} \left(w - \frac{1}{w}\right)^2 - A + \xi\Big\}^{1/2}}{(w^2 - 1 - A + \xi)\left\{\left(w - \frac{1}{w}\right)^2 - A + \xi\right\} + \left(w - \frac{1}{w}\right)^2 + \frac{A}{w^2} - \frac{\xi}{w^2} + \dfrac{B\left(w - \frac{1}{w}\right)^2\left(1 + \frac{1}{w^2}\right)}{2\xi}} \quad \cdots \quad (8)$$

Conditions of Reflection of Waves.

In the absence of the magnetic field,

$$\mu^2 = \delta = \frac{w^2 - 1}{w^2}$$

and

$$\frac{1}{U} = \frac{\delta^{1/2}}{c}\left[1 + \frac{1}{w^2 - 1}\right] = \frac{1}{c\delta^{1/2}}$$

or

$$U = c\delta^{1/2} = \mu c.$$

Hence the group velocity vanishes when $\mu = 0$ and the condition of reflection is the same as that obtained by putting $\mu = 0$.

In the presence of a magnetic field we can write

$$\frac{U}{c} = \frac{Z}{D},$$

where

$$Z = \left[w^2 - 1 - A \pm \left\{\left(w - \frac{1}{w}\right)^2 B + A^2\right\}^{1/2}\right]^{3/2}\left[\left(w - \frac{1}{w}\right)^2 - A \right.$$
$$\left. \pm \left\{\left(w - \frac{1}{w}\right)^2 B + A^2\right\}^{1/2}\right]^{1/2} \quad \cdots \quad (9)$$

$$D = \left[w^2 - 1 - A \pm \left\{ \left(w - \frac{1}{w} \right)^2 B + A^2 \right\}^{1/2} \right] \left[\left(w - \frac{1}{w} \right)^2 - A \right.$$

$$\left. \pm \left\{ \left(w - \frac{1}{w} \right)^2 B + A^2 \right\}^{1/2} \right] + \frac{A}{w^2} \mp \frac{\left\{ \left(w - \frac{1}{w} \right)^2 B + A^2 \right\}^{1/2}}{w^2}$$

$$+ \left(w - \frac{1}{w} \right)^2 \pm \frac{B \left(w - \frac{1}{w} \right)^2 \left(1 + \frac{1}{w^2} \right)}{2 \left\{ \left(w - \frac{1}{w} \right)^2 B + A^2 \right\}^{1/2}} \quad \cdots \quad (10)$$

The upper sign in Z and D gives one wave and the lower sign gives the other wave. The group velocity vanishes when any one of the two factors of Z is equated to zero. Hence we obtain reflection when

$$w^2 - 1 - A \pm \left\{ \left(w - \frac{1}{w} \right)^2 B + A^2 \right\}^{1/2} = 0 \quad \cdots \quad \cdots \quad (11.a)$$

or

$$\left(w - \frac{1}{w} \right)^2 - A \pm \left\{ \left(w - \frac{1}{w} \right)^2 B + A^2 \right\}^{1/2} = 0 \quad \cdots \quad \cdots \quad (11.b)$$

Taking the condition (11.a) we have

$$-(w^2 - 1 - A) = \pm \left\{ \left(w - \frac{1}{w} \right)^2 B + A^2 \right\}^{1/2} \quad \cdots \quad \cdots \quad (11.a')$$

or

$$(w^2 - 1)^2 - 2A(w^2 - 1) = \left(w - \frac{1}{w} \right)^2 B$$

or

$$(w^2 - 1) \left[w^2 - 1 - 2A - \frac{B}{w^2} (w^2 - 1) \right] = 0.$$

Hence equation (11.a) is satisfied when

(1) $w^2 - 1 = 0$, i.e. $w = 1$ $\quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (12.a)$

or   (2) $w^4 - w^2(1 + 2A + B) + B = 0$,

substituting for w, A and B, we get

$$\frac{p^4}{p_0^2} - \frac{p^2}{p_0^2} \left(1 + \frac{p_H^2}{p_0^2} \right) + \frac{p_L^2}{p_0^2} = 0$$

or

$$p_0^2(p^2 - p_L^2) = p^2(p^2 - p_H^2)$$

or

$$p_0^2 = p^2 \frac{p^2 - p_H^2}{p^2 - p_L^2} \quad \cdots \quad \cdots \quad \cdots \quad (12.b)$$

By substituting these values of w^2 in (11.a') we can easily see that $w = 1$ refers to the positive sign on the right hand side of (11.a') and the value of p_0^2 given by (12.b) refers to the negative sign.

We thus find that Z vanishes when we take the upper sign $(+)$ and put $w = 1$. But it is easy to see that the corresponding expression for the denominator also vanishes and we have

$$\frac{U}{c} = \frac{0}{0} \text{ which is (indeterminate)}.$$

Putting $w = 1 + \epsilon$ were ϵ is a small quantity of the first order, we can show that $\frac{U}{c} \to 0$ as $\epsilon \to 0$. We thus conclude that the group velocity of the wave given by the upper sign vanishes, when $w = 1$. The group velocity of the other wave vanishes when

$$p_0{}^2 = p^2 \frac{p^2 - p_H{}^2}{p^2 - p_L{}^2} \cdot \cdot \qquad \cdot \cdot \qquad \cdot \cdot \qquad \cdot \cdot \quad (12 \cdot b)$$

Taking the condition $(11.b)$ we get

$$-\left\{ \left(w - \frac{1}{w} \right)^2 - A \right\} = \pm \left\{ \left(w - \frac{1}{w} \right)^2 B + A^2 \right\}^{1/2}.$$

It is easy to see that for the positive sign before the radical in the above equation it is satisfied when $w = 1$. It is now evident that this condition also gives the same condition for the vanishing of the group velocity of the wave given by the upper sign as the condition $(11.a)$. Taking the negative sign, the roots are given by

$$\left(w - \frac{1}{w} \right)^2 = (2A + B)$$

$$\text{i.e.} \quad w - \frac{1}{w} = \pm (2A + B)^{1/2} \quad \cdot \cdot \qquad \cdot \cdot \qquad \cdot \cdot \quad (13)$$

This gives

$$\left. \begin{aligned} w &= \frac{\sqrt{(2A + B) + 4} + (2A + B)^{1/2}}{2} \\[2mm] \text{and} \qquad w &= \frac{\sqrt{(2A + B) + 4} - (2A + B)^{1/2}}{2} \end{aligned} \right\} \quad \cdot \cdot \qquad \cdot \cdot \qquad \cdot \cdot \quad (13')$$

We thus conclude that while there is only one condition for the reflection of the wave given by the upper sign in the expression for $\frac{U}{c}$ there are four conditions for the reflection of the other wave given by

$$\left. \begin{aligned} &(1) \quad p_0{}^2 = p^2 \frac{p^2 - p_H{}^2}{p^2 - p_L{}^2} \\[2mm] &(2) \quad w = \frac{\sqrt{(2A + B) + 4} + (2A + B)^{1/2}}{2} \\[2mm] &(3) \quad w = \frac{\sqrt{(2A + B) + 4} - (2A + B)^{1/2}}{2} \end{aligned} \right\} \quad \cdot \cdot \qquad \cdot \cdot \qquad \cdot \cdot \quad (14)$$

Thus we see that for one of the waves the conditions of reflection is independent of the earth's magnetic field.   This particular wave we will call the ' ordinary '.

We take (2) and (3) first.   It can be shown that this leads to the usually accepted condition for reflection of the extraordinary wave, for taking (13), and substituting the value of A and B we get

$$\left(w - \frac{1}{w}\right) = \pm \frac{p_H}{p_0}.$$

Now we have

$$w = p/p_0,$$

and

$$\frac{p}{p_0} - \frac{p_0}{p} = \pm \frac{p_H}{p_0}$$

or

$$p^2 - p_0{}^2 = \pm p p_H$$

or

$$p^2 = p_0{}^2 \pm p p_H$$

or

$$p_0{}^2 = p^2 \mp p p_H.$$

The electron concentration at which the ordinary is reflected is given by

$$N_0 = \frac{mp^2}{4\pi e^2} \qquad .. \qquad .. \qquad .. \qquad .. \quad (15)$$

The electron concentration at which the extraordinary is reflected is given by

$$N_e = \frac{m}{4\pi e^2} \left(p^2 \mp p p_H\right).$$

The extraordinary thus can be reflected from two electron concentrations given by

$$\left.
\begin{array}{ll}
(1) & N_e = \frac{m}{4\pi e^2} \left(p^2 - p p_H\right) \\[2mm]
(2) & N_e = \frac{m}{4\pi e^2} \left(p^2 + p p_H\right)
\end{array}
\right\} \qquad .. \qquad .. \qquad .. \qquad .. \quad (16)$$

In the case of the extraordinary, the electron density given by the first of the above values is the usually accepted value.   Regarding the value of N_e corresponding to the positive sign (2) it was supposed so long that this could not be detected as this kind of reflection would take place at a height higher than the one at which reflection process (1) and the reflection for the ordinary ray takes place.   But Toshniwal and Pant [6] in this laboratory obtained three reflections, the highest of which was interpreted by Toshniwal [7] to correspond to process (2).   This interpretation has been further experimentally verified by Leiv Harang [8] working at Tromsø by photographing the (P', f) curve.

We shall now examine the other two conditions.   These are not obtained when we obtain the conditions of reflection by putting $\mu = 0$.   Taking the condition (1) we observe that

$$p_H{}^2 > p_L{}^2$$

We have then, when $p > p_H$,

$$p_0^2 = p^2 \frac{1 - p_H^2/p^2}{1 - p_L^2/p^2}$$

$$= p^2 - p_T^2 \text{ approximately} \quad .. \quad .. \quad (17)$$

When $p_H > p > p_L$, p_0 is imaginary.

When $p_L > p$, it can be shown that the condition refers to the reflection of the ordinary wave and

$$p_0^2 = p^2 \frac{p_H^2 - p^2}{p_L^2 - p^2} \quad .. \quad .. \quad .. \quad .. \quad (18)$$

From (17) we have for short waves

$$N_e = \frac{m}{4\pi e^2} (p^2 - p_T^2) \quad .. \quad .. \quad .. \quad .. \quad (19)$$

We will thus have in general the following conditions of reflection :

$$p^2 = p_0^2 \ldots\ldots \text{ordinary wave}$$

$$\left.\begin{array}{l} p^2 - pp_H = p_0^2 \\ p^2 + pp_H = p_0^2 \\ p^2 - p_T^2 = p_0^2 \text{ approx.} \end{array}\right\} \text{extraordinary wave} \quad .. \quad .. \quad (20)$$

For short waves there will be three conditions for the reflection of the extra-ordinary wave and only one condition for the reflection of the ordinary wave. These are given by

$$p^2 = p_0^2 \ldots\ldots \text{ordinary waves}$$

$$\left.\begin{array}{l} p^2 - pp_H = p_0^2 \\ p^2 + pp_H = p_0^2 \\ p^2 - p_T^2 = p_0^2 \text{ approx.} \end{array}\right\} \ldots \text{extraordinary} \quad .. \quad .. \quad (20')$$

Of the three extraordinary reflections we may observe one, two or all the three reflected pulses depending upon the intensity of the reflections. Unfortunately a purely ray treatment cannot give us any indication of these intensities. If the reflection corresponding to the layer given by the condition

$$p^2 - pp_H = p_0^2$$

is quite strong and can be observed, the ordinary and extraordinary penetrating frequency will be related by the equation

$$p_2^2 - p_2 p_H = p_1^2,$$

where
$$p_1 = 2\pi\nu_1,$$

and
$$p_2 = 2\pi\nu_2$$

and ν_1 and ν_2 are the ordinary and extraordinary penetrating frequencies, the difference between them being ·7 megacycles approximately.

If, however, this reflection is weak and cannot be observed and we are observing the reflection from the layer corresponding to the relation

$$p^2 - p_T{}^2 = p_0{}^2,$$

the relation between the ordinary and extraordinary penetrating frequencies is given by

$$p_2{}^2 - p_T{}^2 = p_1{}^2.$$

From this the difference between the ordinary and extraordinary penetrating frequencies comes out (taking the ordinary penetrating frequency to be 4 Mc./sec.) to be 0·13 Mc./sec. for Allahabad.

If instead of using this approximation we use the exact formula (17), the difference between the penetration frequencies comes out to be 0·135 Mc./sec. for Allahabad. This result shows that we are justified in taking the above approximation.

The experimentally observed value of the difference between the ordinary and extraordinary penetrating frequencies has so far been reported to be about 0·7 Mc./sec. by workers all over the world as well as in the Allahabad laboratory. In addition, Messrs. Pant and Bajpai have several times observed this difference to be only about 0·14 Mc./sec. This result which at first appeared to be very puzzling admits of an easy explanation on the above theory.

For England where the horizontal component of the earth's magnetic field is only 0·18 Gauss (i.e. only half of the value at Allahabad), when the critical penetration frequency is 4 Mc./sec. and absorption is small, this difference will be only 0·05 Mc./sec. and it may be difficult to observe.

It may be observed that we can write (18) as

$$p_e{}^2 - p_0{}^2 = p_T{}^2$$

i.e. $(p_e - p_0)(p_e + p_0) = p_T{}^2$

or $(p_e - p_0) = \dfrac{p_T{}^2}{2p_0}$ approx.

This shows that even when p_T is large the difference between the penetration frequencies will be the smaller, the larger the value of the penetration frequency for the ordinary. To get an appreciable difference, therefore, the observations should be at a time when the penetration frequency is small, i.e. when the ion concentration is small.

RELATION BETWEEN THE GROUP AND PHASE VELOCITIES.

In the absence of friction and magnetic field the product of wave and group velocities is c^2. When a magnetic field is present, we get

$$\frac{UV}{c^2} = \frac{(w^2-1-A+\xi)^2}{(w^2-1-A+\xi)\left\{\left(w-\frac{1}{w}\right)^2-A+\xi\right\}+\left(w-\frac{1}{w}\right)^2+\frac{A}{w^2}-\frac{\xi}{w^2}+\dfrac{B\left(w-\frac{1}{w}\right)^2\left(1+\frac{1}{w^2}\right)}{2\xi}}$$

$$= \frac{(w^2-1-A+\xi)}{\left(w-\frac{1}{w}\right)^2-A+\xi-\frac{1}{w^2}+\dfrac{w^2-1+\left\{B\left(w-\frac{1}{w}\right)^2\left(1+\frac{1}{w^2}\right)\right\}\Big/2\xi}{w^2-1-A+\xi}}$$

$$= \frac{1}{1-\frac{1}{w^2-1-A+\xi}+\dfrac{w^2-1+\left\{B\left(w-\frac{1}{w}\right)^2\left(1+\frac{1}{w^2}\right)\right\}\Big/2\xi}{(w^2-1-A+2\xi)^2}} \qquad \ldots \qquad \ldots \quad (21)$$

The formula shows that in general $UV \neq c^2$. We shall evaluate it in some particular cases. When

$$p \gg p_H \text{ and } w \gg 1,$$

we have $\xi = \pm B^{1/2}w.$

Hence neglecting 1 and A in comparison with w, we get

$$\frac{UV}{c^2} = \frac{1}{1-\dfrac{1}{w^2 \pm B^{1/2}w}+\dfrac{w^2 \pm B^{1/2}\frac{w}{2}}{(w^2 \pm B^{1/2}w)^2}}$$

$$= \frac{1}{1-\dfrac{\pm B^{1/2}w}{2(w^2 \pm B^{1/2}w)^2}} \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \quad (22)$$

Hence when $w \gg 1$, i.e. for low electron densities

$$UV = c^2.$$

For smaller values of w, i.e. high electron density, this will not be true. In particular for the ordinary wave when w is very nearly 1, UV is equal to zero.

CONCLUSION.

Starting from the assumption that reflection of radio-waves from the ionosphere takes place when the group vanishes, we have shown above that we get only one condition for the reflection of the ordinary wave, but four conditions for the reflection of extraordinary wave when using long waves. For short waves the conditions for the reflection of the extraordinary wave are three. It has also been shown that the difference between the penetration frequencies for the extraordinary and one of the ordinary waves may have a

small value of the order of ·135 Mc./sec. In addition it has been shown that the product of the group and phase velocities is not always $= c^2$.

I wish to express my sincere thanks to Prof. M. N. Saha, F.R.S. and Dr. G. R. Toshniwal, D.Sc., for their kind interest and encouragement, and to Mr. R. R. Bajpai for helping me with mathematical calculations.

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CHEMICAL ANALYSIS OF INDIAN MEDICINAL PLANTS. THE ACTIVE PRINCIPLE AND OTHER CONSTITUENTS OF *FUMARIA OFFICINALIS* BEDD.

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(Communicated by Dr. S. Dutt.)

(*Read March 25, 1937.*)

Fumaria officinalis Bedd., known in India by the vernacular names ' *Shaheterah* ' or ' *Pitpapra* ' (Hindustani), or ' *Pipara* ' (Bengali), is a common herb belonging to the natural order Fumariacæ. The plant has been in use in the Indian system of medicine for a very long time, being regarded as a diuretic and alterative. Besides, it is known to remove hepatic obstructions and is an aperient and expellent of humours but more especially of atrabiles. It has also been successfully used as a laxative, and is beneficial in dyspepsia depending upon the torpidity of the intestines, and in scrofulous skin affections. The taste of the plant is bitter, slightly acrid and astringent.

As regards its chemical composition, it has been a subject of numerous investigations. Peschier in 1829 (*J. Pharm.*, 1829, *17*, 280) found an alkaloidal principle in it, a fact which was later on corroborated by Hannon (*J. Chem. Med.*, 1852, (3), *8*, 705). The properties of this base which was termed fumarine were later on described in minor detail by Bettandier (*Pharm. Ztg.*, 1885, *24*, 542) and also by Reichwald (*ibid.*, 1889, *28*, 161). The drug was also supposed to contain fumaric acid and salts (Peschier, *loc. cit.* ; Wincler, *Ann.* 1833, *4*, 230 ; Trommodorf, *J. Pharm.*, 1833, *25*, 152). Wehmer (*Die Pflazenstoffe*, 1931) mentions that Schlotterbeck (*Amer. Chem. Jour.*, 1900, *24*, 249) and also Schmidt (*Arch. Pharm.*, 1901, *239*, 401) showed that fumarine is probably identical with protopine. However, no reference to the latter work is found in abstracted chemical literature. Pictet (*Vegetable alkaloids*, 1913) retains the name fumarine and says that it crystallizes in prisms m.p. 199°C., has the formula $C_{21}H_{19}NO_4$ and is optically active.

The Indian variety of *Fumaria officinalis* was examined in this laboratory by Pendse and Dutt five years ago (*Ind. J. Med. Res.*, 1932, *22*, 663), but they could not isolate the alkaloid. Since the plant is successfully used in India in native medical practice, it was deemed proper by the present author to re-investigate the problem and to test the claims of the Western workers in view of the work of Pendse and Dutt with regard to the Indian variety. As a result of the present research, it has now been definitely shown that the drug contains 1% of inorganic salts, consisting of a mixture of potassium nitrate (70·9%) and potassium chloride (29·1%) ; a hydrocarbon 0·5% which has been identified

as penta-triacontane $C_{35}H_{72}$ and an alkaloidal principle (0·13%) identical with protopine ; besides tannins, phlobaphenes and sugars.

The presence of penta-triacontane in this drug is of sufficient interest in view of the hypothesis put forward by Channon and Chibnall (*Biochem. J.*, 1929, *23*, 168) regarding the metabolism and formation of paraffins in plants. According to their view the paraffins are formed from the fatty acids *via* the ketone. Stearone, the ketone derived from stearic acid, which is one of the most abundant fatty acids found in nature, on reduction will give pentatria-contane according to the scheme below :—

$$C_{17}H_{35} . COOH \longrightarrow C_{17}H_{35} - CO - C_{17}H_{35} \longrightarrow C_{35}H_{72}$$
(Stearic acid)   (Stearone)   (Penta-triacontane)
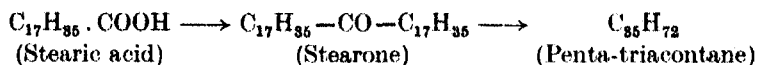
The diuretic properties of the drug are mainly due to the presence of such large quantities of potassium salts. Protopine, which was originally isolated from opium, has been found to exist widely in nature especially in plants belonging to the natural orders, Papaveraceæ and Fumariaceæ, e.g. *Macleya cordata, Stylophorum diphyllum, Sangunaria canadensis, Chelidonium majus* and *Corydalis veruyi.* It is a strong base and has powerful physiological properties. Protopine resembles cryptopine but solutions of the salts of the former have a bitter taste. In small doses protopine acts on frogs as a narcotic and in stronger doses paralyses the muscle-substance and the peripheral ends of the nerves. Upon mammals it has a poisonous action like that of camphor, but differs from it in paralysing the circulating organs. It has been isolated from *Fumaria officinalis* in the form of its acetate after the removal of tannins, inorganic and waxy materials, and is the active principle responsible for the physiological action of this drug.

EXPERIMENTAL.

The material used in these investigations was collected from the neighbourhood of Jhansi District (U.P.), dried in the shade and the entire plant, minus the roots, was crushed finely in an iron mortar. A weighed sample of this powdered material was exhaustively extracted in a Soxhlet's apparatus using different solvents when the following amounts of the extracts dried at 100° to constant weight were obtained :—

Benzene Extract.—A waxy-green mass was obtained which consisted mostly of chlorophyll and a white crystalline stuff of low melting point embedded in it. Yield 3·3%.

Chloroform Extract.—A yellowish green sticky mass smelling of sugars and giving reactions for alkaloids was obtained. Yield 4·5%.

Alcoholic Extract.—A yellow semi-solid mass containing some brown crystalline mass was obtained. It gave a yellow precipitate with lead acetate, a green colour with alcoholic ferric chloride and reduced Fehling's solution. Gave reactions for alkaloids. Yield 13·1%.

Aqueous Extract.—A brownish crystalline residue was obtained consisting of organic salts, giving tests for nitrates and chlorides. Reduced Fehling's solution and gave faint precipitates with alkaloidal reagents. Yield 5·1%.

2·5 kilograms of the well powdered material was then repeatedly extracted with boiling ethyl alcohol several times, in a big extraction flask of five litre capacity. The extracts were filtered hot and on cooling deposited a flocculent white crystalline precipitate. This was filtered and the dark green alcoholic extractive was concentrated whereby on cooling a further crop of the crystalline mass was obtained. The two crops were mixed together, and washed several times with warm alcohol, till a dirty white crystalline mass (A) was obtained containing a tinge of greenish colour. The washings were added to the alcoholic mother liquor.

The mother liquor from this mass, consisting of a thick syrupy liquid, was then further concentrated, the final concentrations being done in a vacuum dessicator under a very high vacuum. The semi-solid residue thus obtained was then extracted several times with hot benzene, under a reflux condenser, till the benzene extracts were perfectly colourless. Benzene removed all the chlorophyll and waxy material, and the mass then assumed a brownish-yellow appearance. The combined benzene extracts, on the complete removal of the solvent, gave a hygroscopic dark green mass, which on repeated washings with cold ethyl alcohol gave a dirty white amorphous residue which was added to the crystalline mass (A) obtained before.

The original alcoholic extract obtained after the removal of chlorophyll and wax through benzene was then dissolved in about one litre of alcohol. At this stage a little amount of white crystalline inorganic substance was left behind, which did not go into solution even on boiling. This was also added to the crystalline mass (A). The alcoholic solution was then treated with an alcoholic solution of lead acetate in order to free it from tannins and colouring matter. A flocculent yellow precipitate of the lead salt was formed, which was filtered over a filter pump, washed thoroughly with alcohol, suspended in ethyl alcohol and decomposed by passing a current of purified hydrogen sulphide. The filtrate obtained, after the separation of lead sulphide, was then concentrated under reduced pressure. A thick brownish-yellow residue was obtained, which failed to give any crystalline stuff and answered to all reactions of tannins. It was extracted with different solvents but no chemically pure substance could be isolated from it.

The clear alcoholic solution obtained, after removal of the lead lake, was then freed from excess of lead in the usual manner and concentrated to a small volume. A little acetic acid was added and the solution left for about a fortnight when fine silky needles separated out which were filtered and washed with small quantities of ethyl alcohol. The white crystalline needles (B) gave reactions for alkaloids and melted at 247–250°C. after previous shrinking at 237°C.

The mother liquor was again concentrated and gave a further yield of the acetate of the alkaloid which was filtered, washed and added to the first (B) The syrupy residue left behind was then dissolved in pure distilled water and on examination was found to contain a large amount of reducing sugars. A sample on treatment with phenyl-hydrazine gave an osazone (m.p. 206°C.), which was identified as glucasazone, showing the presence of glucose in the plant.

Examination of the crystalline mass (A).

Isolation of Potassium nitrate and potassium chloride.—The crystalline mass obtained as described above was dehydrated carefully in a vacuum dessicator over anhydrous calcium chloride, powdered finely and extracted repeatedly with hot boiling benzene. Benzene removed the organic matter leaving behind a dirty brownish-white amorphous inorganic material. This was dissolved in a small quantity of water, boiled with animal charcoal and filtered. On cooling the aqueous solution, a mixture of long needles and rhomblic plates was obtained. A further quantity was obtained on concentrating the mother liquor to a very small volume (total yield, 27·5 gms., i.e. 1·1% on the weight of dried drug). This was identified to be a mixture of potassium nitrate and potassium chloride. An estimation of the chloride content of this mixture gave 27·16 per cent of potassium chloride and 72·84 per cent of potassium nitrate. (2·0214 grams of the mixture gave 1·5561 grams of AgCl ; 27·16 per cent KCl requires 1·5562 grams of AgCl.)

Isolation of penta-triacontane.—The benzene extracts were concentrated to a very small volume and on being allowed to cool and stand, a large amount of crystalline matter began to separate. This was filtered and recrystallized several times from benzene and petroleum ether, till finally a white crystalline mass was obtained melting at 70–73°C. The final crystallizations were done through large volumes of ethyl alcohol several times, till colourless small needles were obtained (yield 13 grams) melting at 75-76°C. and the melting point did not rise further on subsequent crystallization. The compound which gave reactions for a hydrocarbon was identified to be penta-triacontane. It is a colourless, tasteless and odourless crystalline substance, which burns with a non-smoky luminous flame, giving a characteristic odour of burnt paraffin. It is soluble readily in benzene, less so in petroleum ether, alcohol, methyl alcohol and glacial acetic acid and insoluble in water. It distills unchanged at 329-331°C. at 15 m.m. pressure. It does not decolourize bromine in chloroform. (Found C, 85·19, 85·02 ; H, 15·01, 14·71 ; M.W. (Ebullioscopic in benzene) 479, 504, 489 ; $C_{35}H_{72}$ requires, C, 85·36 ; H, 14·64% M.W. 492.)

Examination of the alkaloidal content (B).

The crystalline acetate of the alkaloid obtained as described above was recrystallized twice from boiling ethyl alcohol till fine silky needles were obtained melting at 267°C. These were then dissolved in about 200 c.c. of boiling distilled water, cooled and treated with dilute solution of sodium hydroxide,

when the liberated base separated out in the form of gelatinous white precipitate. This was allowed to settle and then filtered. On crystallization from absolute methyl alcohol, small needles were obtained melting at 200–202°C. This was then recrystallized from a mixture of ethyl alcohol and chloroform when colourless needles were obtained melting at 206-207°C. (Yield 4·3 grams). It is extremely bitter and gives a beautiful violet colouration with a reddish tinge, which becomes blood red on standing with con. sulphuric acid, and a light reddish-violet colour with con. H_2SO_4 containing a little $K_2Cr_2O_7$. With con. H_2SO_4 and $KClO_3$ it gives a deep orange red colour and a very light yellow with concentrated HNO_3. With Frohde's reagent a very intense violet colour turning to olive green is developed. With Mendelins' reagent the crystals turn violet, and yield a green solution which becomes blue and finally violet. With phosphotungstic acid a white precipitate is formed and with phospho-molybdic acid a yellow precipitate. With K I and I_2 a flocculent brown precipitate and with tannic acid a flocculent white precipitate is obtained. With Mayer's reagent a flocculent white precipitate is obtained. It gives a yellow precipitate with gold chloride and platinic chloride. It is optically inactive. It gave no colour with ferric chloride and was insoluble in caustic alkalis. (Found C, 67·72, 67·59 ; H, 5·44, 5·52 ; N, 3·5, 4·00 $C_{20}H_{19}O_5N$ requires C, 67·99, H, 5·38 N, 3·97%.) From all its reactions and elementary analysis it has been identified to be protopine.

Protopine hydro-chloride.—Protopine (1 gram) was dissolved in the minimum quantity of absolute alcohol and treated with gaseous hydrochloric acid. On adding ether to the solution the hydrochloride separated out as fine colourless crystalline powder, m.p. 274°C. (Found Cl 9·00 ; $C_{20}H_{19}O_5N$ HCl requires Cl 9·18%.)

Protopine acetate.—Protopine (1 gram) was treated with the requisite amount of glacial acetic acid in alcohol. On standing the acetate crystallized out in fine needles, which were filtered, washed with alcohol and recrystallized from the same media when colourless silky needles were obtained, m.p. 268°C. (Found C, 63·72 ; H, 5·79 ; $C_{20}H_{19}O_5N$. $CH_3CO\cdot OH$ requires C, 63·92, H, 5·57%.)

Protopine picrate.—Protopine (0·5 gram) was dissolved in water and treated with an aqueous solution of picric acid whereby a flocculent yellow precipitate of the picrate was formed. It was filtered, washed and recrystallized from glacial acetic acid when micro-crystalline deep yellow needles were obtained, m.p. 249°C. (decomp.).

CHEMICAL EXAMINATION OF *CLEOME PENTAPHYLLA* LINN.
PART II. CONSTITUENTS OF THE OIL FROM THE SEEDS.

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(Read March 25, 1937.)

In a previous communication on the subject Misra and Dutt,[1] in the course of their investigations on the chemical constituents of *Cleome pentaphylla* Linn. (N. O. Capparideae), isolated from it a substance of the nature of a lactone called by them cleomin, and reported that the drug also contains an oil to the extent of 22%. A few constants of this oil were previously determined by Hooper (*Ann. Rept., Indian Museum, Industrial Section*, 1908-09). Hooper found that it had Acid Value 6·4 ; Saponification Value 194·6 ; and Iodine Value 119·5. This appears to be all the work done on the fatty constituents of this highly medicinal drug. A systematic examination of the oil was undertaken by the present authors and forms the subject of this communication.

The three constants found by Hooper appear to be in fairly good agreement except for the acid value. These, as determined by the present authors, were found to be Acid Value 36·5 ; Saponification Value 194 ; and Iodine Value 122·6. As these represent the mean of several determinations conducted with all precautions, they are more reliable.

It was not found practicable to determine the proportion of unsaturated acids in a quantitative manner, as even on repeated attempts at bromination no crystalline bromo-derivatives could be separated. Qualitatively, however, the presence of oleic and linolic acids has been proved and is described in detail in the experimental part.

EXPERIMENTAL.

Extraction of the oil.—2 kg. of the seeds were obtained from the neighbourhood and finely crushed in an iron mortar, having previously been dried in the shade. The crushed mass was then extracted exhaustively with benzene in a large extraction flask. The benzene extracts were collected together and the solvent removed by distillation when an oil of a light green colour was left (446 gms.), having a faint odour of mustard. The oil was then purified with animal charcoal and Fuller's earth. Even on prolonged keeping no sediment or crystalline matter was deposited.

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[1] *Proc. Nat. Inst. Sci. India*, Vol. III, p. 45, (1937).

Examination of the oil.—The oil contained no nitrogen or sulphur and was optically inactive. It burned with a partially sooty and colourless flame and a thin film exposed to the air in the laboratory resinified in a few days, indicating that it belongs to the class of semi-drying oils. Table I gives its physical and chemical constants.

TABLE I.

Specific Gravity	..	..	.. 0·9268 at 20°C.
Refractive Index	..	..	.. 1·4653 at 25°C.
Solidification Point		..	.. —12°C.
Acid Value ..	..	..	.. 36·5.
Saponification Value	..	..	.. 194.
Iodine Value ..	..	..	.. 122·6.
Acetyl Value ..	..	..	.. 33·5.
Hehner's Value	..	..	.. 91·5.
Unsaponifiable Matter	..	..	.. 2·08%.

150 gms. of the oil were saponified with alcoholic caustic potash and the soap extracted with ether to remove the unsaponifiable matter. It was then dissolved in excess of water and decomposed with dilute sulphuric acid in presence of petroleum ether. The petroleum ether solution of the fatty acids was washed free from traces of sulphuric acid in a separating funnel and left in contact with fused calcium chloride to remove the moisture. It was then filtered and the mixed fatty acids obtained by removal of the solvent by distillation. Table II gives the constants of the mixed fatty acids.

TABLE II.

Consistency ..	..	..	.. Semi-solid.
Liquifying Point	..	..	.. 33–35°C.
Specific Gravity	..	..	.. 0·8873 at 40°C.
Neutralization Value	..	..	.. 188.
Mean Molecular Weight	..	..	.. 298.
Iodine Value ..	..	..	.. 126·5.

The mixed fatty acids (50 gms.) were then separated into saturated (solid) and unsaturated (liquid) acids by Twitchell's lead-salt-alcohol method (Twitchell, *J. Ind. Eng. Chem.*, 1921, *13*, 806). Table III gives the percentage, mean molecular weight, and the iodine values of the saturated and unsaturated acids.

TABLE III.

Acid.			Per cent in mixed acids.	Iodine Value.	Mean Molar Weight.
Saturated ..	..	..	22·4	1·7	259·8
Unsaturated ..	..	..	77·6	139·5	280·3

Examination of Unsaturated Acids.—The quantitative separation of bromo-derivatives according to the method of Eibner and Muggenthalor (*Chem.*

Tech. of Oils, etc., 5th Ed., I, 573) perfected by Jamieson and Boughman (*J. Amer. Chem. Soc.*, 1920, *42*, 1197) was unsuccessful even on repeated attempts. No crystalline products could be obtained. The following qualitative method was therefore adopted.

Oxidation with potassium permanganate.—10 gms. of the unsaturated acids were dissolved in aqueous caustic potash and a 2% solution of potassium permanganate added in a thin stream with constant stirring, till the pink colour became persistent indicating the end of the oxidation process. A current of sulphur dioxide was next passed into the mixture to dissolve the precipitated manganese dioxide. The products of oxidation were thus left in the form of soft white flocculent flakes that settled down. The precipitate was filtered, washed with water, and extracted with ether. The ethereal extract on removal of the solvent by evaporation deposited a white crystalline solid which on further purification and recrystallization from alcohol melted at 131-32°C. and was identified as dihydroxy-stearic acid. This established the presence of oleic acid in the mixture of unsaturated acids. The ether insoluble product of oxidation was next extracted with a large volume of boiling water repeatedly and on cooling deposited white minute crystals which on recrystallization from water melted at 164-65°C. These were found to be tetra-hydroxy-stearic acid as the melting point with an authentic sample remained undiminished at 164-65°C. The formation of this acid on oxidation proves conclusively the presence of linolic acid in the mixture.

The filtrate from the oxidation products was reduced to about 1/15th its volume by evaporation, made alkaline with dilute caustic soda, and neutralized with dilute sulphuric acid. It was then extracted with ether. The ethereal extract was washed repeatedly with small quantities of water and then dried by keeping it in contact with anhydrous calcium chloride. On removal of ether by evaporation a white crystalline deposit was left behind. This was purified by recrystallization from water and ethyl alcohol successively and identified as azelaic acid of m.p. 106°C. This acid is always formed as a bye-product of such oxidation. The presence of hexahydroxy-stearic acid could not be proved conclusively which shows that linolinic acid is either absent or present only in minute traces.

The iodine value of the mixed fatty acids was 139·5. Since linolinic acid can only be present in very minute traces, if at all, it may be regarded for all practical purposes that the mixture of the unsaturated acids consists of oleic and linolic acids alone. The proportion of these acids can be calculated with the help of the following two equations :

$$X + Y = 100 \ldots (i).$$
$$90·07X + 181·14Y = 100 \times 139·5 \ldots (ii).$$

where X represents percentage of oleic acid :

and Y represents percentage of linolic acid :

Table IV gives the percentages of these acids calculated by this method.

TABLE IV.

Acids.			Per cent in unsat. acids.	Per cent in mixed acids.	Per cent in oil.
Oleic	..	..	..	45·2	35·07	32·02
Linolic	..	..	..	54·8	42·53	38·97

Examination of Saturated Acids.—These were freed from traces of un-saturated acids by pressing over a porous plate and obtained in a white solid form melting at 52-58°C. The mixture of saturated acids was converted into methyl esters by dissolving in absolute methyl alcohol and passing a current of dry hydrogen chloride till the solution became saturated. It was then refluxed over a water bath for 18 hours. The mixed esters were treated with sodium bicarbonate and washed with water and extracted with ether. The ether extract was washed and dried and the esters recovered by removal of ether by evaporation.

The methyl esters thus obtained were subjected to fractional distillation under highly reduced pressure and the boiling points and the pressure of various fractions was noted. Their iodine and saponification values were determined and the mean molecular weights calculated. These were found to range between 270·3 and 298·4 which are the molecular weights of methyl palmitate and stearate respectively, except the residue whose mean molecular weight was found to be 300·2. This indicates the presence of a higher acid namely arachidic acid. The percentages of the acids were calculated in various fractions by means of their iodine and saponification values.

Table V gives the results of distillation and Table VI those of analysis.

TABLE V.

Fraction.		B.P.	Pressure.	Weight in gms.
I	..	150–55°C. rose to 165°	5 mm.	0·71
II	..	165–68°C. rose to 175°	Do.	3·27
III	..	175-76°C. rose quickly to 183°	Do.	3·28
IV	..	183–90°C. rose to 200° and above.	Do.	2·28
Residue	..	above 200°C.	Do.	2·35

TABLE VI.

Fraction.	Iodine value.	Saponification value.	Mean M.W.	Acids.							
				Palmitic gm. per cent.		Stearic gm. per cent.		Arachidic gm. per cent.		Unsaturated gm. per cent.	
I	1·25	203·5	275·7	0·47	66·2	0·19	26·7	..	..	0·006	0·89
II ..	1·37	200·6	279·7	2·01	64·8	1·05	33·9	..	..	0·032	0·98
III ..	1·87	198·2	283·1	1·65	50·3	1·33	40·5	..	..	0·045	1·34
IV ..	3·28	193·5	189·9	0·60	26·3	1·19	52·2	..	..	0·053	2·35
Residue	20·28	186·9	300·2	..	..	0·95	40·4	0·22	9·7	·341	14·54
				4·73		4·71		0·22		0·477	

The percentages of various acids in saturated acids and the oil is given below, Table VII.

TABLE VII.

Acids.				Per cent in saturated acids.	Per cent in original oil.
Palmitic	..	..	..	46·69	9·57
Stearic	..	..	..	46·47	9·53
Arachidic	..	..	..	2·15	0·44
Unsaturated	..	..	..	4·69	69·45

Examination of unsaponifiable matter.—This was extracted from the oil by ether extraction after saponification, in the form of a white waxy material. It was purified by repeatedly crystallizing from ethyl alcohol and finally gave a phytosterol of m.p. 131-32°C.

SUMMARY.

The oil from the seeds of *Cleome pentaphylla* Linn. has been analysed and found to consist of glycerides of the following :—

Palmitic Acid	..	..	.. 9·57%.
Stearic ..	..	..	.. 9·53%.
Arachidic Acid	..	..	.. 0·44%.
Oleic Acid	..	..	.. 32·02%.
Linolic Acid	..	..	.. 38·97%.
Unsaponifiable matter, a phytosterol		..	2·08%.

COLOUR VISION: NORMAL AND ABNORMAL, FOR PHYSICISTS.

By W. BURRIDGE, *Physiology Laboratory, Lucknow.*

In the past the subject of colour vision was one of the most difficult with which the medical student had to deal. Doubtfully could the subject be called a science because the student of it found that he could do little more than consider a mass of incompatible theories, each of which seemed equally as valid as any other, and select from them some one which pleased him best. Workers in this field also had their scope limited. They might find new facts, but, having found them, their aim seemed to be to find the already existing theory with which the new facts seemed best compatible.

It now appears that the difficulties of this subject were not provided by the facts, but by certain preconceived notions with which the facts were expected to conform. Those who dealt with colour vision presumed that the natural stimulation by light of the nervous elements in the retina was a process exactly similar to that of exciting a piece of excised nerve by an electric current. In addition, none of them knew how a beating heart, and with this rhythmically active structures generally, behave when they are stimulated. The scientist who has this knowledge, however, can immediately recognize that the behaviour of the nervous elements of the eye on stimulation is similar to that of a beating heart. And such a recognition so completely transforms the subject of colour vision that, instead of elaborating complicated theories about it, an elementary knowledge of physics enables one to predict its chief phenomena. We can use, in fact, the known phenomena of sound to teach us something about colour.

From what we know about sound, a rhythmically active living nervous structure could be expected to possess the capacity to provide two types of sensation, the one provided by the intensity of each individual effort, the other by the rate of repetition of those same efforts. That is to say, we should expect a rhythmically active nervous structure to provide one sensation mediated by amplitudes and corresponding to loudness, and another mediated by rates and corresponding to the musical note. The phenomena of vision corresponding to loudness and tone are brightness and colour. Hence we conceive the possibility that colour is dependent on the rate of beat of living rhythmical structures.

Acceptance of this possibility makes coloured light an external force which is capable of altering the rates of the rhythmical changes that take place

in the structures of the eye reacting to light. These living rhythmical struc-
tures, however, have a normal rate of beat which is determined by their own
intrinsic forces. It is this normal rate which the external forces may alter.
Further, only two types of change are possible, namely, quickening and
slowing.

Now, if one of these external forces quickened a normal rate, n, say, to
$(n+x)$, it is likely that among the slowers there should be one which slowed
the rate to $(n-x)$. If things were so, then the combined action of these two
forces should give no change of rate at all, though they might augment
amplitude.

These simple calculations, expressed in terms of colour, imply that every
colour may have an opposite such that the two acting together neutralize
each other's action on rates. Many of such pairs of colours could conceivably
exist, but their admixture should give a common result.

These deductions are realized. For every colour has an opposite or
complementary colour such that the admixture of each pair gives the common
result of grey or white according to strength. Hence we find that the neutral
colour is grey, and that this can become white by amplitude increase. Further
evidence in support of this is derived from the behaviour of hearts. Drugs
which can alter both rate and amplitude have been found by me to alter
amplitude only when they are employed in weak concentrations. If this rule
hold true for rhythmical structure generally, then feeble light should exhibit
variations of brightness of the neutral colour only. This is also true, for
dim light gives us variations of grey.

The next expectation derived from what is known about sounds is that
every colour should be mediated by a range of rates and not by a single rate.
If we take as the standard for C a vibration rate of 256, say, there will be a
range of vibrations on either side of this which we must still call C. Some
of these we cannot directly distinguish from our standard, others we shall still
call ' C ' but declare that they are somewhat flat or sharp as the case may be.
If, next, rates are gradually quickened from the standard, we shall even-
tually reach a pitch which is more than a sharpened C, but is instead a new
note, C sharp. Similarly on the other side C will gradually flatten to C flat.

The expectation from such facts is that grey through quickening should
gradually sharpen into a colour, grey sharp, and by slowing should flatten into
a colour, grey flat. These two colours should possess the property of mutual
decolourization to grey without the intermediate production of any other
colour, because grey flat can only flatten grey sharp to grey and vice versa.
Two colours with these predictable properties actually exist. They are red
and green. Up to the present, however, their capacity to decolourize one
another has been simply inexplicable. In this case, therefore, we actually
progress from the inexplicable to the predictable.

We may now progress to drawing the colour scale given below (see fig. 1).

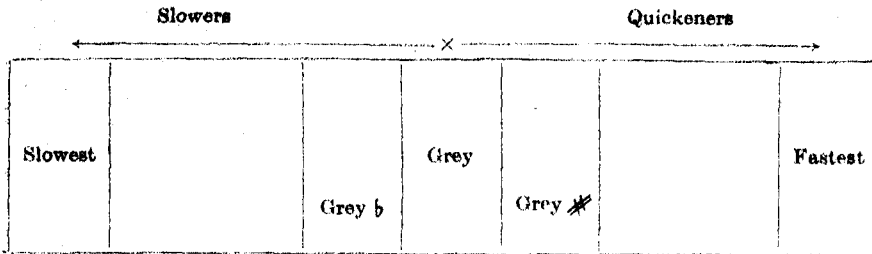|						
Slowest			Grey			Fastest
		Grey ♭		Grey ♯		

Fig. 1.

The scale is given to indicate the existence of two other peculiar colours lying at the extremes of the scale. Their existence is predictable from the fact that our capacity to perceive movement is limited. The limitations are definite; things may move too fast or too slow. There should therefore be at one end of the scale a colour mediated by the slowest rate perceptible to us, and at the other end a different colour mediated by the fastest perceptible rate. These two colours are of opposite nature and in combination with red and green should provide all other colours.

The next task, then, is to search among colour vision theories for one which divides the colours into two pairs of opposites with red-green as one pair. The theory we require is that enunciated by Hering, and from it we find that the other pair is blue-yellow.

These colours require now to be placed in position. Help towards this is provided by the artists who divide colours into the warm and cold. Their actual division has been strongly criticized, both by physiologists as well as physicists, on the basis of spectrum findings with the thermopile. Such criticism has actually been unscientific. If artists do not feel what someone argues from the spectrum that they ought to feel, it is not to be deduced from this that they feel wrongly. One can only deduce from the differences that further investigation is required. An entirely new light is thrown on these matters when one appreciates that the artists have obtained their sensations of warmth and cold from rhythmical structures. In such structures warmth quickens, and cold slows. Consequently we place red and yellow among the quickeners, and blue and green among the slowers. This gives the colour scale below (see fig. 2).

Cold   Warm
Slowers   ×   Quickeners

Blue		Green	Grey	Red		Yellow
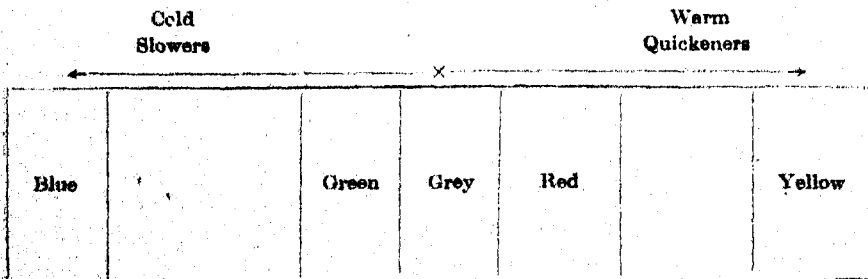
Fig. 2.

It is to be observed that the ' slow ' division of the scale is made longer than the ' quick '. That is done because a mixture of blue and yellow yields green, i.e. blue slows more than yellow quickens.

On looking at the scale we appreciate the possibility that colours may also possess a property corresponding with what musicians term ' pitch '. Hence we look for another inherent property of colours, and find what we want in their intrinsic brightness.

The colour scale above represents the normal state of affairs. From this normal or average only two variations are possible, it may either be harder or easier for rate changes to be effected. The limit of hardness would imply an inability of those external forces, which normals call colour, to quicken or slow rates beyond the range which gives grey. The possessor of such insensitive end-organs would therefore see variations of grey where others see colours, and he would be termed completely colour-blind.

A milder degree of hardness would not permit the weaker external forces, those which normals call red and green, to quicken or slow enough to give a colour distinct from grey. The possessors of such end-organs would there-fore exhibit varying degrees of red-green colour-blindness. Some, for example, would confuse all reds with grey, others would be able to distinguish ' sharp ' reds from grey, but not the ' flat ' reds, and so on. The converse would hold for green. These predictions are in general fulfilled.

A quite different type of colour-blindness would arise from the possession of unduly labile end-organs. In such, the rates would be quickened and slowed so much by yellow and blue, respectively, that the rates actually produced by these forces would be either too fast or else too slow for the existence of motion to be perceptible. The individuals possessing such labile end-organs would consequently be ' blind ' to yellow and blue. The normality of the end-organs at the periphery of the retina is the possession of this degree of lability.

The main facts of colour vision and colour blindness are thus predictable from the standpoint that the end-organs which give rise to visual sensation have an inherent rhythmical activity. Conversely, of course, the facts lead to a theory that the end-organs possess this inherent rhythm. In the past, however, every scientist who thought on these matters started out with a pre-supposition that the end-organs of the retina had an essentially different character from that which they actually possess. This presupposition placed the science of colour vision in a position analogous to that of astronomy in the days when it was presupposed that the earth was stationary and flat.

If we could imagine a group of intelligent scientists speculating on the phenomena of sunrise from the bases of a stationary and flat earth, is to be appreciated that seemingly satisfactory explanations would be forthcoming. We could even expect the three schools of those who are suggested that the sun was pushed from behind, of those who suggested that it was pulled from the front, and of those who suggested that it had an inherent power of movement. It would further be impossible to make definite choice between these different

schools. Each one's theory would be as valid as that of any other, a point to which we would draw special attention.

When any false theory is accepted as a fact, it becomes possible, by correlating it with other facts, to build up a number of other false theories each of seemingly equal validity with its fellows. Such has been the character of the divers theories hitherto elaborated around the phenomena of colour vision. Their seeming equal validity is in itself the evidence that they each treat as fact some fundamental false theory. The fundamental theory which we have found to be false is the one that presupposes that the stimulating action of light on the retinal end-organs is the same as the action of electric currents on a piece of excised nerve.

But even if we still believe in this fundamental proposition, the advance of the science of muscle and nerve shows that traditional colour vision theories are faulty. It was good physiology, for example, in the days of Helmholtz to believe that an individual nerve or muscle fibre gave graded responses when it was excited by graded strengths of electric current. Now we know instead that such responses have an all or nothing character. Each individual element gives either its full response or none at all. Such responses, it should be noted, are similar to those of a gun cartridge.

The sensitive layer of the retina consists of individual nervous elements. Consequently, if their condition and stimulation were as hitherto presupposed, their responses to stimulation should possess an all or nothing character similar to that of a gun cartridge. This would make all vision consist of areas of dazzling brightness interspersed by areas of complete blackness. Our vision obviously is not so, but it only 'ought' to be so if the presuppositions were true.

If anyone, then, makes this assumption of partial stimulation, he must either reconsider his fundamental proposition or provide still another adjustive hypothesis. In contrast with this, response graded according to the strength of stimulation is a typical character of the responses of rhythmical structures. The grading of response that actually occurs is, in fact, another line of evidence that rhythmical structures are being stimulated.

The final point to be noted about colour vision is that the past science was founded on what the psychologists call an error of projection. Everyone believed at one time that grass is green. We now know instead that the green is in us. But when it came to putting the green inside us, the existence of a special green sensitive structure was imagined to exist in the retina. This supposition now appears to have been as much an error of projection as was the supposition of the presence of the green in the grass. Colour appears instead to be our interpretation of rhythmical activity arising from a particular source just as the musical note is our interpretation of the same type of activity arising from a different source. The interpretive instrument is common to both and provides that fundamental relation between music and colour which is realized in the Moonlight Sonata.

RADIO STUDIES OF THE UPPER ATMOSPHERE AT ALLAHABAD.

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(Communicated by Prof. M. N. Saha, F.R.S.)

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1. INTRODUCTION.

The necessity of a thorough study of ionized regions of the upper atmosphere for a complete understanding of the problem of propagation of radio waves is now well recognized all over the world. Important investigations have been carried out in higher latitudes, and a considerable amount of data has been collected. The condition of the ionosphere is expected to be rather different in equatorial and tropical regions, and hence for the thorough understanding of the problem it is essential to collect data for these regions too. Realizing this, work has been started in India at Calcutta and at Allahabad. A considerable amount of data has now been collected at Allahabad, which is briefly presented here.

2. THEORETICAL.

The problem has been theoretically studied by Appleton,[1] Goldstein [2] and Hartree,[3] and more recently Booker [4] has given an interesting exposition of the subject. But starting from the original dispersion equation given by Appleton it will be shown here, as has been already pointed out by one of us [5] (G. R. Toshniwal) that the expressions for the absorption of radio waves are opposed to those obtained by Booker. Derivation of the various formulæ needed for the explanation of the experimental observations is therefore given here.

The dispersion equation for vertical propagation of radio waves is given by

[1] Appleton, *Jour. Inst. Elec. Eng.*, Vol. 71, p. 642, (1932).
[2] Goldstein, *Proc. Roy. Soc.*, Ser. A, Vol. 121, p. 260, (1928).
[3] Hartree, *Proc. Camb. Phil. Soc.*, Vol. 27, p. 143, (1931).
[4] Booker, *Proc. Royal Soc.*, Ser. A, Vol. 150, p. 267, (1935).
[5] Toshniwal, ' Absorption in the Ionosphere ', *Science and Culture*, Vol. 2, p. 277, (1936).

$$c^2 q^2 = 1 + \cfrac{1}{(\alpha + i\beta) - \cfrac{\gamma_T^2}{2(1 + \alpha + i\beta)} \cdot \cfrac{\pm 1}{(1 + \alpha + i\beta)} \sqrt{\left[\frac{\gamma_T^2}{2}\right]^2 + \gamma_L^2 (1 + \alpha + i\beta)^2}} \qquad .. \quad (1)$$

$$= \left(\mu - \frac{ick}{p}\right)^2 = 1 + \frac{1}{X + iY}$$

where,

cq = complex refractive index of the wave.

$$\alpha = -\frac{p^2 m}{Ne^2} - a. \qquad \beta = \frac{mvp}{Ne^2}. \qquad \gamma_T = \frac{pH_T}{cNc}. \qquad \gamma_L = \frac{pH_L}{cNc}.$$

p = angular frequency of the radio wave.

H_L, H_T are the longitudinal and transverse components of the earth's magnetic field, N is the number of electrons per c.c. and v is the collisional friction frequency per electron per second.

' a ' is the Lorentz polarization term.

For short waves the necessary condition for reflection is

$$cq = 0 \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (2)$$

Thus as long as $v \ll p$, we can easily prove from (2) and (1) that

$$1 + \alpha = 0 \quad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (3)$$

$$1 + \alpha = \pm \gamma \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (4)$$

where $\quad \gamma = \sqrt{\gamma_T^2 + \gamma_L^2} \quad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (5)$

Equation (3) is obtained by using the positive sign before the radical in equation (1) and represents the condition for reflection of the ordinary wave, while equation (4) gives the condition for reflection of the extraordinary ray.

Equation (3) and (4) can be written in the form

$$N_0 = \frac{mp^2}{e^2(1-a)} = 1.24 \times 10^{-8} f_c^2 \qquad .. \qquad .. \qquad .. \qquad .. \qquad (3a)$$

$$N_e = \frac{1}{1-a} \cdot \frac{mp^2}{e^2} \left[1 \pm \frac{p_H}{p}\right] = 1.24 \times 10^{-8} \left[1 \pm \frac{p_H}{p}\right] f_c^2 \quad .. \quad (4a)$$

where N_0 represents the number of electrons per c.c. just sufficient for the reflection of the ordinary ray and N_e the number for the extraordinary ray, $p_H = \dfrac{He}{mc}$, and f_c is the critical penetration frequency. In evaluating the numerical value in (3a) and (4a) the Lorentz polarization term has been taken to be zero.

3. REFLECTION AND ABSORPTION.

The dispersion theory shows that the effect of absorption can be expressed in terms of an absorption coefficient k, such that the ratio of the intensity of the emergent wave to that of the incident wave is given by

$$\frac{E}{E_0} = \exp. \left[-\int k \, dh\right] = \rho \qquad .. \qquad .. \qquad .. \qquad (6)$$

where ρ is the reflection coefficient and h is the thickness of the absorbing layer.

From (1) we get

$$\mu^2 - \left(\frac{ck}{p}\right)^2 = 1 + \frac{X}{X^2 + Y^2} \quad .. \qquad .. \qquad .. \quad (7)$$

and

$$\frac{2\mu ck}{p} = \frac{Y}{X^2 + Y^2} \quad .. \qquad .. \qquad .. \quad (8)$$

The values of X and Y can be easily calculated from (1), if we make the following assumptions—

Case I :—

$$\frac{\gamma_T^4}{4(1 + \alpha + i\beta)^2 \gamma_L^2} \ll 1$$

Case II :—

$$(1 + \alpha + i\beta)^2 \ll 1$$

For case (I) it can be easily proved that

$$\left. \begin{array}{l} X = \alpha \pm |\gamma_L| \\ Y = \beta \end{array} \right\} \quad .. \qquad .. \qquad .. \qquad .. \quad (9)$$

where positive sign is to be used for the ordinary ray and the negative sign for the extraordinary ray.

For case II, we get,

$$\left. \begin{array}{l} X = \alpha \\ Y = \beta \end{array} \right\} \text{ for the ordinary ray} \qquad .. \qquad .. \qquad .. \quad (10)$$

and

$$\left. \begin{array}{l} X = \alpha - \dfrac{\gamma_T^2(1 + \alpha)}{(1 + \alpha)^2 + \beta^2} \\[2mm] Y = \beta \left[1 + \dfrac{\gamma_T^2}{(1 + \alpha)^2 + \beta^2} \right] \end{array} \right\} \text{ for the extraordinary ray} \qquad .. \quad (11)$$

The absorption in the ionosphere may be divided into two parts : (1) absorption in a deviating region where μ approaches zero, and (2) absorption in a non-deviating region where μ is nearly equal to unity.

4. ABSORPTION IN THE DEVIATING REGION.

Assuming that $\mu^2 - 1 \gg \left(\dfrac{ck}{p}\right)^2$, we can prove from (7) and (8) that

$$\frac{ck}{p} = -\frac{1}{2} \cdot \frac{Y}{X} \left[\frac{1}{\mu} - \mu \right] \qquad .. \qquad .. \qquad .. \quad (12)$$

Since the ray has to travel twice through the absorbing region the integrated absorption coefficient is given by

$$2 \int_{\mu=1}^{\mu=0} k\, dh = -\frac{p}{c} \frac{Y}{X} \int_{\mu=1}^{\mu=0} \left[\frac{1}{\mu} - \mu \right] dh$$

$$= -\frac{p}{2c} \frac{X}{Y} [P' - P] \qquad .. \qquad .. \qquad .. \quad (13)$$

where

$$P' = 2 \int_{\mu=1}^{\mu=0} \frac{dh}{\mu} \text{ and } P = 2 \int_{\mu=0}^{\mu=1} \mu \, dh$$

P' is called the group path and P is called the optical path. Usually $P' \gg P$, then in place of (13) we get approximately

$$2 \int_{\mu=1}^{\mu=0} k \, dh = -\frac{p}{2c} \frac{Y}{X} P' \quad .. \quad .. \quad .. \quad (14)$$

Now the ordinary ray is reflected from the region where $1+\alpha = 0$ and the extraordinary ray usually from the region where $1+\alpha = -\gamma$. Hence the quasi-transverse conditions—Case II—hold good for the region from which the ordinary ray is reflected, and the quasi-longitudinal conditions—Case I— are approximately valid for the region from which the extraordinary ray is reflected, even at places such as Allahabad, where θ, the angle between the vertical and the earth's magnetic field, is nearly $45°$.

Thus for evaluation of the value of X and Y we have to use equation (10) for the ordinary ray and equation (9) for the extraordinary ray. Hence the integrated absorption coefficient is given by

$$2 \int_{\mu=1}^{\mu=0} k \, dh = -\frac{p}{2c} \cdot \frac{\beta}{\alpha} P' = \frac{\nu}{2c} P_0', \quad .. \quad .. \quad (15)$$

for the ordinary ray, and

$$2 \int_{\mu=1}^{\mu=0} k \, dh = -\frac{p}{2c} \frac{\beta}{\alpha - |\gamma_L|} = \frac{\nu}{2c} \frac{p}{p+|p_L|} P_x' \quad .. \quad (16)$$

for the extraordinary ray, where

$$|p_L| = \left| \frac{eH_L}{mc} \right|$$

and is independent of the sign of e and H.

From (15), (16) and (6) we find that

$$\frac{ln \, \rho_x}{ln \, \rho_0} = \frac{p}{p+|p_L|} \cdot \frac{P_x'}{P_0'} \quad .. \quad .. \quad .. \quad (17)$$

where ρ_x and ρ_0 are the reflection coefficients for the extraordinary ray and the ordinary ray respectively, and P_x' and P_0' represents the group path for the extraordinary ray and the ordinary ray respectively.

Thus per unit group path (17) shows that as far as the absorption in the deviating region is concerned the extraordinary ray will be less absorbed than the ordinary ray.

In place of (17) Booker gets the following for unit group path

$$\frac{ln \, \rho_x}{ln \, \rho_0} = \frac{p}{p-|p_L|} \quad .. \quad .. \quad .. \quad .. \quad (17a)$$

which shows that the extraordinary ray will be absorbed more than the ordinary ray in the deviating region.

5. ABSORPTION IN THE NON-DEVIATING REGION.

In this region, the collisional friction frequency ν is expected to be large, and hence for all values of θ lying between $0°$ and $45°$, the quasilongitudinal conditions will hold good. Hence when μ is unity from (8) and (9) we find that

$$k = \frac{1}{2} \cdot \frac{p}{c} \cdot \frac{Y}{X^2 + Y^2}$$

$$= \frac{p}{2c} \cdot \frac{\beta}{(\alpha \pm |\gamma_L|)^2 + \beta^2} \qquad .. \qquad .. \qquad .. \quad (18)$$

whence the ratio of the absorption coefficient for the extraordinary and the ordinary ray at the same height is given by

$$\frac{k_x}{k_0} = \frac{\left(-p + \dfrac{eH_L}{mc}\right)^2 + \nu^2}{\left(-p - \dfrac{eH_L}{mc}\right)^2 + \nu^2}$$

$$= \frac{[p - |p_L|]^2 + \nu^2}{[p + |p_L|]^2 + \nu^2} .. \qquad .. \qquad .. \qquad .. \quad (19)$$

In place of the above formula Booker obtains

$$\frac{k_x}{k_0} = \frac{[p + |p_L|]^2 + \nu^2}{[p - |p_L|]^2 + \nu^2} \qquad .. \qquad .. \qquad .. \quad (19a)$$

It follows immediately from (18) that in the non-deviating region the extraordinary ray will experience greatest absorption at a height corresponding to $\nu = p + |p_L|$ i.e. $\beta = \left| \alpha - |\gamma_L| \right|$, while the ordinary will be most absorbed where $\nu = p - |p_L|$ i.e. $\beta = \left| \alpha + |\gamma_L| \right|$. Thus we see that the absorption for the extraordinary ray will begin at much lower heights, and hence the range of integration for calculating the total absorption will be more in the case of the extraordinary than in the case of the ordinary ray.

6. EXPERIMENTAL RESULTS.

Study of the ionosphere was started at Allahabad [1] (Long. $81° 55' 0''$, Lat. $25° 25' 55''$) early in 1934. The transmitter has been designed on the lines suggested by Appleton and Builder.[2] The receiving set consists of a two

[1] Toshniwal and Pant, *Nature*, Vol. 133, p. 947, (1934).
[2] Appleton and Builder, *Proc. Phys. Soc.*, Vol. 44, p. 76, (1932).

valve S.G. transformer—coupled high frequency amplifier, an anode bend rectifier, and one stage D.C. low frequency amplifier. Since the time constant of the receiving circuit was kept extremely low, it was possible to keep the transmitter and the receiver side by side. The reflected pattern was seen on a cathode-ray oscillograph using a linear time base. Two oscillographs were usually employed, one of them was used for photographic purposes, while the other was employed for visual observations. The transmitting aerial consisted of a five wire system.[1] The length of the wires was $\frac{3}{4}\lambda$ for 45, 55, 75, 90 and 110 metres. A combination of earth screen and a buried earth plate has been used for earthing purposes. This arrangement was quite satisfactory for the present investigations.

Equivalent height measurements.—The virtual height of the reflecting region was measured usually at a constant frequency. It has been found that during the day, the average height of the F and the E regions is 250 and 110 kms. respectively. Occasionally reflections have been observed from the intermediate regions with equivalent heights of about 140 kms. (E') and 180 kms. (F_1 ?).

The magnetoionic split doublet echoes have always been seen in the early mornings a few minutes before ground sunrise and at night a few hours after sunset. The time of appearance of the doublet echoes in the morning was very nearly fixed, but the split echoes in the night would appear at any time about two hours after sunset. At times triplet echoes apparently belonging to the same system[2] and corresponding to the two equations (3) and (4) have been observed.

7. COMPLEX ECHOES.

In addition to the usual reflections a jumble of peaks consisting of several closely spaced echoes facing in and out were visible on rare occasions in place of any one of the multiple reflections. Such complex echoes have been observed and discussed by Appleton and Builder,[3] Ratcliffe and White[4] and others. But so far we have not come across any detailed study. Therefore, it is thought necessary to describe in detail the complex echoes observed by us. Automatic recording and visual observations were made simultaneously and the following description is based on both :—

Two interesting records of complex echoes are reproduced in figs. 1 and 2 and two photographs of echoes are reproduced in figs. 3 and 4.

Fig. 1 shows a record of equivalent height at 4 Mc/sec. between 1700 and 2200 on 14th March, 1936. There were four multiple echoes from 1830 to 2000, three from 2000 to 2100 and five between 2100 and 2130. The

[1] Gilliland, *Proc. Inst. Rad. Eng.*, Vol. 22, p. 236, (1934).

[2] Toshniwal, *Nature*, Vol. 135, p. 437, (1935).

[3] Appleton and Builder, *Proc. Phys. Soc.*, Vol. 45, p. 208, (1933).

[4] Ratcliffe and White, *Phil. Mag.*, Vol. 16, p. 125, (1933).

virtual height of all the multiple echoes went on increasing and was maximum at about 1945 after which the second echo as seen visually suddenly became a little broad and there appeared in it two to three peaks almost superimposed. After two or three minutes the first echo too followed the same process and then the whole of the space between the first echo and the second multiplet was filled with echoes rapidly fading in and out. Sometimes echoes which were just visible above the time base line could be seen visually even in the

INDIAN STANDARD TIME

1700   1800   1900   2000   2100   2200

kms.

1200

800

400

Ground pulse
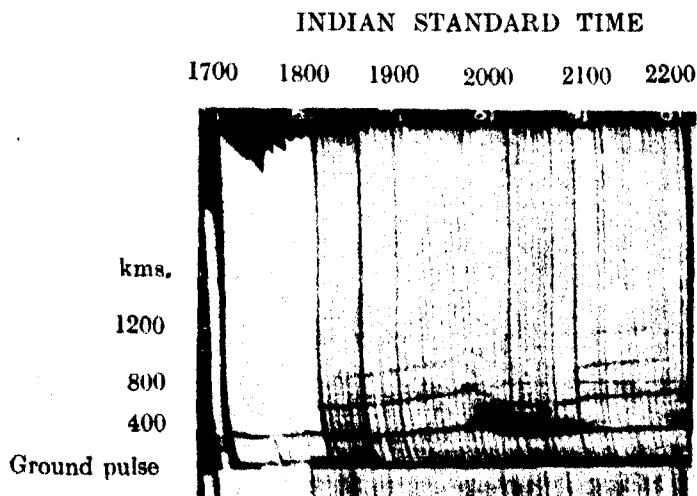
14th March 1936

Fig. 1.

space between the 2nd and the 3rd reflections. At 2007 strong reflections from E region were also seen which lasted for two minutes only and hence no trace in the record could be found. There was maximum complexity near about 2000 after which the intensity of the peaks gradually became smaller and smaller and a few minutes after 2100 simple echoes were left. It is remarkable that only the first echo was complex, the rest were all simple. After 2100 the virtual height again began to increase and a few minutes before 2200 the complexity again suddenly started. Fig. 3 is a photograph of the complex-echo taken at 2215 on March 14, 1936. At this time the first echo alone was complex.

    In order to study the phenomenon in detail another record was taken in which the photographic paper was moved more rapidly. Fig. 2 shows the record of complex echo obtained between 2230 and 0030. The beginning of the ground pulse is not seen. The first black horizontal line at the beginning of the record shows the first F-echo which is complex. At 2312 the time base
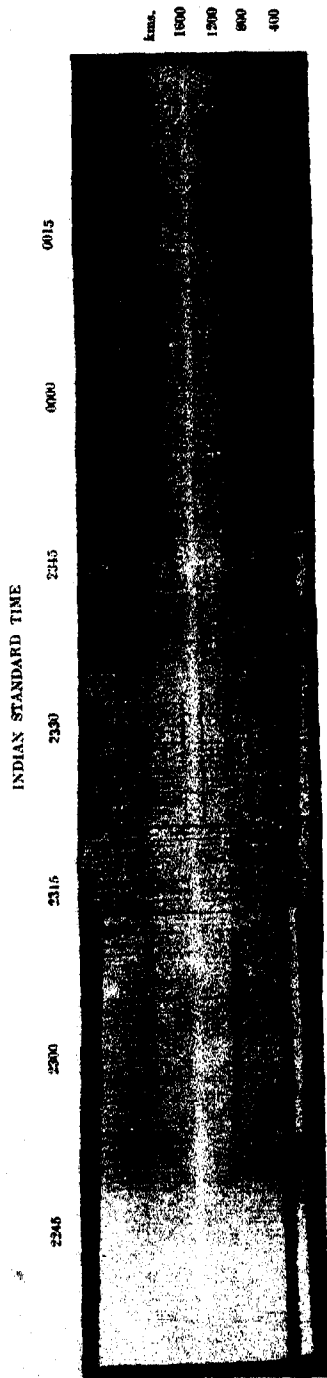
kms. 2000 1600 1200 800 400

INDIAN STANDARD TIME

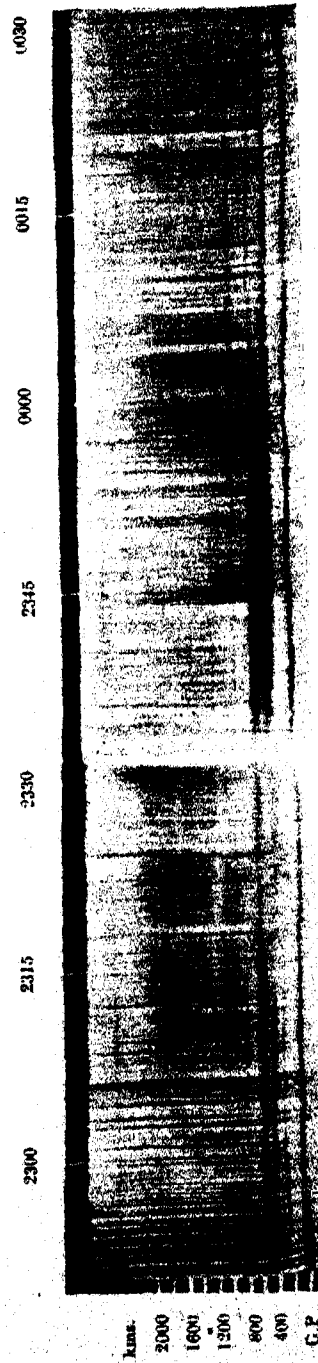FIG. 2.

kms. 2000 1600 1200 800 400 G.P

FIG. 5.

became unstable and the pattern was elongated a little. Stable conditions were, however, reached at 2317. There were several peaks in between the first echo and 2nd multiple echo. From the very beginning two complex separate echoes are seen in the first order reflection. The complexity however slowly decreased after about 2320.

Later one of the two said echoes is seen slowly heading towards the 2nd multiple echo. This shows that even when other peaks had subsided, one of them was strong, and the equivalent height went on increasing. In addition to the first F echo, four more multiple echoes were present between 2320 and 2340. The presence of another horizontal line above the fifth multiple echo *shows a reflection from 1720 km.* and evidently this is not a multiple echo. Near 2330 a seventh horizontal line shows another echo reflected from *2016 km.* The difference in kms. between the 6th and the 7th echo is exactly equal to the equivalent height of the F-echo.

Normal conditions were restored after 0015 I.S.T. No record was taken afterwards but visual observations were continued. Strong echoes from E-region were seen from 0020. At this time composite echo from E-region also was observed. Fig. 4 shows five photographs taken at an interval of one minute each, the first reflection from E is seen to be complex, and the space between the first and second order F-reflections is full of various echoes.

Fig. 5 shows another example of a complex echo observed near midnight of 2nd April. The first black horizontal line shows the ground pulse. The other black lines represent echoes from F layer (281 kms.). The first echo and the second echo were both fairly strong at 2300, after which the first echo became gradually weak and the second multiple became gradually complex, as will be seen from the thickness of the line. Near about 2320, first multiple echo also became complex and both of them remained complex up to 2355, after which the first alone remained complex up to 0020 and then it bifurcated
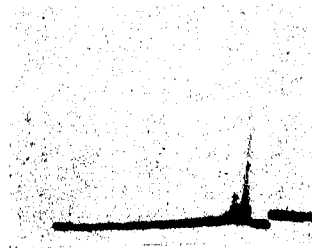

FIG. 3.

into two echoes seen till the end of the record. Between 2330 and 2345, in addition to two complex echoes, three other simple multiple echoes were present.

The third multiple echo is present up to the end of the record. The complexity of the second multiple echo disappeared near about 2355, after which it became feeble for about ten minutes. Visual observations taken simultaneously showed that it was not the case of mere broadening of echoes and that the first two echoes actually consisted of several peaks rapidly fading in and out. One thing, however, is to be noted that in the beginning of the record the distance between the ground echo and first reflection is less than that between the 1st and 2nd reflections, while in the end the reverse is the case. Observations had to be discontinued after 0100 I.S.T.

Fig. 6 shows another interesting record taken on 27th February, 1935. On this day also the conditions in the ionosphere were much disturbed and complex echoes were seen for a considerable time before the record was taken. In the record also some remnants of complexity are visible. Throughout the record two orders of reflections from F region at an equivalent height of 375 km. are seen. Another reflection from a virtual height of 172 km.

FIG. 4.

was received almost continuously. Besides feeble echoes at other times in between the 1st and 2nd F-echoes, a strong reflection from an equivalent height of 467 km. was observed from about 0115 to 0120. It is to be noted that it is neither an M echo nor an $E+F$ echo and seems to be due to partial reflection and refraction from an ionized region at such a height.

In addition to the dates given above, complex echoes have been seen on the 3rd, 4th, 10th and 12th December, 1935 and on the 25th February, 1936. On the 4th December, 1935 and 14th March, 1936, even the E echo was found to be complex.

On rare occasions innumerable echoes have been observed. It is very difficult to assign any particular region which gives rise to these echoes. Fig. 7 shows the conditions on December 4, when the ionosphere seems to be

most disturbed. Several multiple reflections together with complex echoes were seen coming from both the E and the F-regions. The shaded portion of the graph shows the presence of various peaks, where equivalent height measurements were uncertain.

Time of disappearance of echoes during the night : The 75 metre waves ceased to be reflected from the ionosphere comparatively much later during December, 1935 and January, 1936, than during the same period in 1934-35.[1]

8. GROUP RETARDATION SPLITTING.

The two magnetoionic components can be separated due to two causes, viz. : (1) stratification splitting, and (2) group retardation splitting. This point has been fully discussed by Appleton and Builder [2] and it is now well established that in the former type of splitting the ordinary ray is the longer delay component and in the latter type the extraordinary is the longer delay component. This type of splitting has been observed by various workers [3] and it is expected that the splitting will be most pronounced when the transmitted frequency is very near the critical penetration frequency of the layer lower than the one from which the echoes are being observed.

We have found that even when the transmitted frequency is quite far from the critical penetration frequency of the lower layer, the group retardation splitting of the echoes is quite considerable. Fig. 8 shows the variation of the equivalent height with wavelength for the two components observed on the 13th April, 1936, between 1826 and 1832 I.S.T. The observations were repeated soon after and no change was found in the curve. It is seen that as the wavelength increases the separation between the two components becomes more and more, and at the same time the longer delay extraordinary component becomes comparatively feebler and feebler. Above 122 metres the extraordinary ray was invisible, while the ordinary was fairly strong. Since the transmitter could not be tuned above 150 metres no reflection from the E-layer appeared. On other occasions, however, we have observed that after the disappearance of the extraordinary ray, on further increasing the wavelength, E-echoes would appear. This type of splitting has been usually seen in the afternoon, when the critical penetration frequency of the E-layer has fallen down to about 2·5 Mc./Sec.

9. IONIZATION OF THE E-LAYER.

The noon critical frequency of the E-layer on December 23 and December 24, 1935 was found to be 4·5 Mc./Sec. and 4·0 Mc./Sec. respectively.

1 Bajpai, *Proc. Nat. Acad. Sc. India*, Vol. 6, p. 40. (1936).
2 Appleton and Builder, *loc. cit.*
3 Ratcliffe and White, *loc. cit.*

10. ABSORPTION.

Measurement of reflection coefficient for both the ordinary and the extra-ordinary rays have been made at a constant frequency of 4 Mc./Sec. and have been described in detail elsewhere.[1]   A brief summary is, however, given here.

It has been found that at times the reflection coefficient is as much as 2. Similar results have also been found by White.[2]   At night when the splitting was just visible, so that the group path P was nearly the same for the two rays, the extraordinary ray has been always found to be stronger than the ordinary ray.   During the day when the group retardation splitting was visible it was found that the extraordinary component was always weaker than the ordinary component.

The reflection coefficient curves for the ordinary and the extraordinary ray when the splitting was due to group retardation have been found to be similar, i.e. the two rays have been found to increase or decrease simultaneously. In the early part of the night when stratification splitting has taken place, the intensity of the echoes did not increase or decrease in step, i.e. if the intensity of the extraordinary ray decreased the intensity of the ordinary ray could increase.   Late in the night, however, when ionization in the lower regions had become very small, the intensity of the two rays was found to increase or decrease simultaneously.

11. COLLISIONAL FRICTION FREQUENCY.

From equation (15) we find that

$$ln\ \rho_0 = \frac{\nu}{2c}\ P'$$

therefore theory demands that if we plot in ρ_0 against the equivalent height $\left(\dfrac{P'}{2}\right)$, a straight line should result from which ν can be found out. This has been found to be approximately true for the F-region in the night, especially when the reflected echoes were comparatively calm, i.e. great intensity fluctuations were not taking place.   Fig. 9 shows the variation of $\log_{10} \rho_0$ with equivalent height, whence ν comes out to be $1\cdot2 \times 10^4$ per electron per sec.   The average value of ν also comes out to be the same.[3]
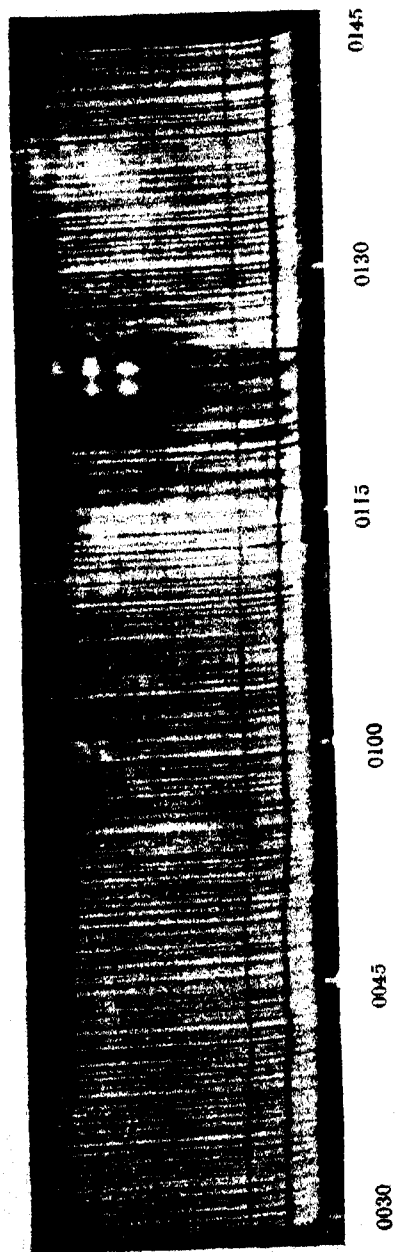
12. DISCUSSION OF THE EXPERIMENTAL RESULTS.

Complex echoes.—Our experimental results show that we can explain the presence of complex echoes on the hypothesis of stepped structure of the

1 Toshniwal, Pant, Bajpai and Verma, *Proc. Nat. Acad. Sc. India*, Vol. 6, p. 161, (1936).

2 White, *Proc. Phys. Soc.*, Vol. 46, p. 805, (1934).

3 Toshniwal, Pant and Bajpai, *Nature*, Vol. 138, p. 37, (1936).

27th February 1936

FIG. 6.

ionosphere. It seems that we have to assume several closely situated strata of ionized regions, where the ionization gradient is not smooth. The radio wave is partially reflected and partially refracted from each of these strata giving rise to several echoes lying close together. The quick changes in the intensity of the peaks seem to be due to sudden changes in the number of electrons. Schafer and Goodall [1] have noticed step-like structure of the F-region ' indicating remarkable abrupt ionic density gradients at heights near 200, 240, 280 kms.'. This type of structure according to Schafer and Goodall had been noticed only during the day light hours. At Allahabad one [2] of us (R. R. Bajpai) has noticed after sunset in December, 1934 fine structure of the E-layer having three ionized regions at 95, 105 and 120 kms. A similar fine structure of the E-layer has also been noticed by Messrs. Ratcliffe and White [3] and also by Watson Watt. [4]

The hypothesis of stepped structure put forward here for the explanation of the complex echoes finds support from fig. 2 and fig. 5. Fig. 2 shows that when the complexity near the first order reflection was slowly decreasing, the virtual height of one of the echoes—a member of the complex echoes—slowly went on increasing after 2320, till it became very feeble near about 0005 and finally disappeared near about 0015. A similar type of separation of one of the members of the complex echoes is also visible in fig. 5 between 0010 and 0030. This separation was visually observed to increase up to 0045, after which it became feeble. It seems that in both these cases, the number of electrons in the region above the F-region was slowly decreasing and hence the equivalent height of the echo was slowly increasing, till too few electrons were left for reflecting the waves. In addition to these, we find that on 2nd April (fig. 5) not only the first but the second echo as well was complex, which also supports our view of production of the complex echoes.

The presence of ionized layers above the F-region finds support further from fig. 6, since here we find echoes showing an equivalent height of 467 kms. for a short period from 0115 to 0120.

At times, however, it has been noticed during the night that each of the two magnetoionic echoes consists of more than one component. To explain this and also the value of ρ greater than unity, it seems that we have to assume an undulatory structure [5] of the reflecting region. The presence of such a structure will give rise to random scattering of the radio wave, and will thus contribute to the complexity of the echoes. Unless more data about complex echoes is collected and correlated with meteorological data, it seems impossible to name the agency responsible for creating circumstances favourable for the production of the complex echoes.

[1] Schafer and Goodall, Nature, Vol. 131, p. 804, (1933).

[2] Bajpai, loc. cit.

[3] Ratcliffe and White, Proc. Phys. Soc., Vol. 46, p. 107, (1934).

[4] Watson Watt, Proc. Roy. Soc., Ser. A, Vol. 141, p. 718, (1933).

[5] Toshniwal, Proc. Nat. Inst. Sci. India, Vol. 1, p. 243, (1935).

4th Dec. 1935

5th Dec. 1935
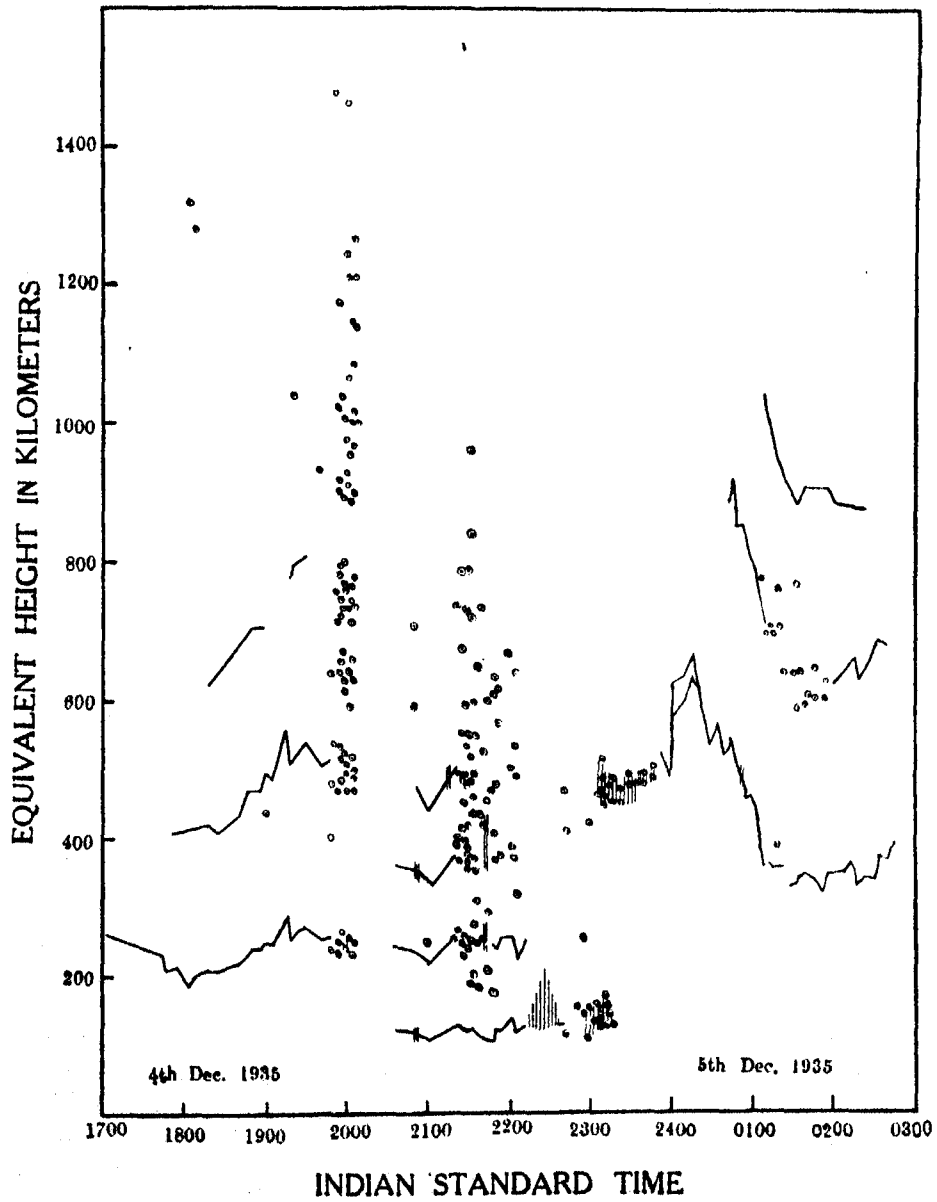
INDIAN STANDARD TIME

Fig. 7.

Absorption.—We see from equations (17) and (19) that theoretically per unit group path the ordinary ray will be more absorbed than the extraordinary ray. The integrated absorption coefficient—which can be calculated from the measurements of the reflection coefficients—of the rays varies directly as the group path of the rays.

Theoretically we conclude that the absorption for the extraordinary, in the lower regions where the refractive index is nearly unity, is maximum near the heights where $\nu = p + |p_L|$, while for the ordinary ray it is maximum where $\nu = p - |p_L|$. Thus for over-all absorption, the range of integration for the extraordinary ray will be larger.

In the night we expect that the ionization in the lower regions will be very little and hence most of the absorption will take place in the deflecting region. Thus we should expect the extraordinary ray to be stronger than the ordinary ray when P'—the group path—is the same for the two rays. This we have found experimentally.

Day time-absorption.—The polarization experiments of Ratcliffe and White [1] show that the extraordinary ray is always weaker than the ordinary ray. Eckersley [2] finds that for shorter wavelengths the extraordinary is stronger than the ordinary ray, while the ordinary is stronger than the extra-ordinary for the longer wavelengths.

These two diametrically opposite views find an easy explanation in the light of our experimental results and theoretical treatment given here.

Fig. 8 shows that even for frequencies far removed from the critical penetration frequency of the lower region, the group retardation splitting is not insignificant.

Thus it seems that the unsplit echo during the day time is due to the balancing effects of the stratification splitting and the group retardation splitting. It has been already mentioned that the group velocity of the extraordinary ray in an ionized region is smaller than the group velocity of the ordinary ray, but the group velocity of the ordinary ray also becomes very small when the critical penetration frequency for the upper region is reached, and hence for such higher frequencies the group path of the ordinary ray may exceed the group path of the extraordinary ray and thus the over-all absorption of the ordinary ray for the higher frequencies may be greater due to this increased group path. At lower frequencies, however, even when the rays are unsplit, the integrated absorption coefficient for the extraordinary ray will be great for two reasons, viz. : (a) due to greater range of integration as absorption begins at lower heights, and (b) considerable group retardation suffered by the extraordinary ray in the lower regions.

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[1] Ratcliffe and White, *loc. cit.*

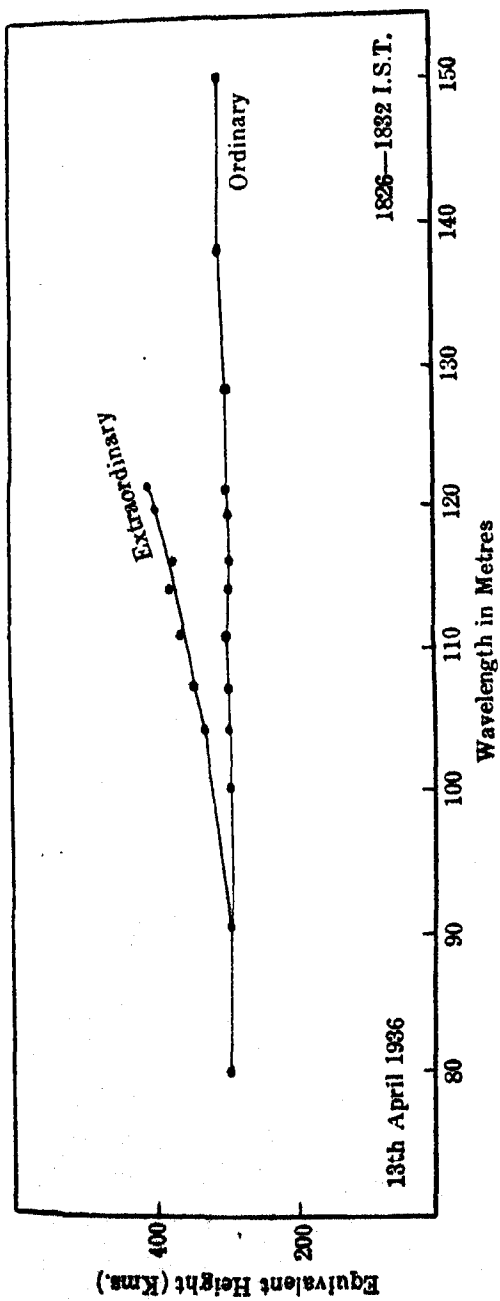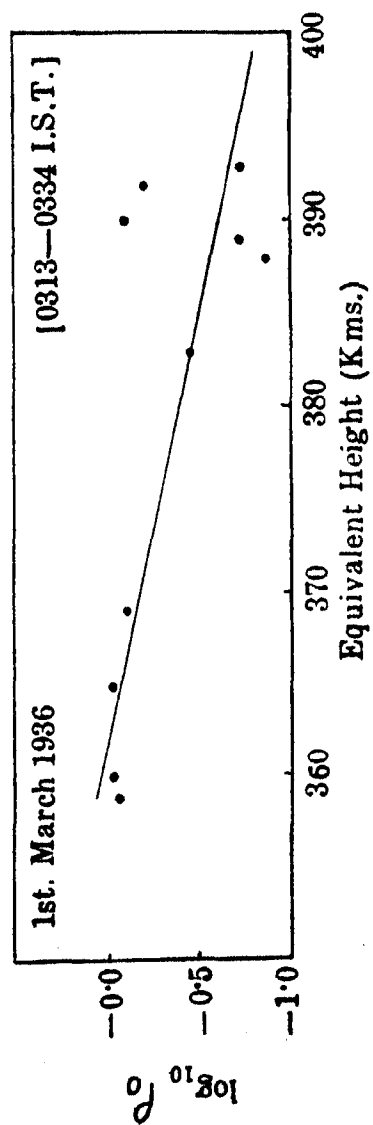[2] Eckersley, *Proc. Roy. Soc.*, Ser. A, Vol. 141, p. 710, (1933).

Fig. 8.

Fig. 9

Contrary to the views held by Farmer and Ratcliffe,[1] it seems to us that the greater absorption of the extraordinary ray during the day is not due to greater absorption in the reflecting region.[2]

Our hearty thanks are due to Prof. M. N. Saha, F.R.S., for his keen interest and constant guidance.

Two of us (Pant and Bajpai) are very grateful to Prof. Saha for the grant of a scholarship out of the Research grant given to him by the Government of the United Provinces.

SUMMARY.

Starting from Appleton's original dispersion equation in Lorentz's notation, it is shown that results for absorption of radio waves are opposed to those obtained by Booker.

Complex echoes have been studied in detail and their occurrence has been explained on the hypothesis of ionized strata lying close to the main reflecting region.

The value of the collisional frequency has been found to be $1 \cdot 2 \times 10^4$ per electron per second.

The two diametrically opposite views of Ratcliffe and White and Eckersley about absorption of Radio waves have been explained in the light of the present work.

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[1] Farmer and Ratcliffe, *Proc. Roy. Soc.*, Ser. A, Vol. 151, p. 370, (1935).

[2] Toshniwal, *Science and Culture, loc. cit.*

THE INFILTRATION OF GOLGI BODIES AND MITOCHONDRIA FROM THE FOLLICULAR EPITHELIUM TO THE EGG.

By D. R. Bhattacharya *and* Murli Dhar Lal Srivastava, *The Zoology Department, University of Allahabad.*

(*Read March 25, 1937.*)

That the nutritive substances required for the growth of the oocyte have to be derived from the surrounding envelopes and transmitted through the egg-membranes is an obvious fact, and has been recognized as such for a long time.

It is only of late, however, that the transmission of some of the inclusions of the follicular cells to the oocyte has been recognized. Brambell (1925) described the infiltration of the Golgi bodies of the follicular cells to the egg periphery in the fowl ; the apparatus, according to him, divides into two, one-half of which passes into the oocyte. Simultaneously, Bhattacharya (1925) described the passage of the Golgi bodies in some reptiles from the follicular cells to the fibrillar layer of the egg through channel-like passages in the zona radiata.

Since then the phenomenon has been found to occur in numerous animals whose oogenesis has been worked out in this laboratory. Bhattacharya, Das, and Dutta (1929) described it in the oocytes of several animals, e.g *Testudo graeca, Calotes versicolor, Columba intermedia, Rana tigrina,* etc. Not only are the Golgi elements transmitted from the follicular cells to the oocyte in these animals but the inclusions of the theca cells, likewise, pass into the follicle cells, to be transmitted later to the oocyte. In some animals, such as *Testudo* and *Kachuga,* the inclusions pass through canalicular passages of the zona radiata. In others, e.g. *Calotes and Uromastix* the large lumps of Golgi bodies pass in a haphazard manner through the zona pellucida to the egg.

P. R. Bhattacharya (1929) who investigated the oogenesis of fishes was able to observe a clear case of infiltration of the follicular Golgi bodies.

D. Narain observed signs of the infiltration of the follicular Golgi bodies in fishes (1930). Narain reported its occurrence also in Amphibia (1930).

In reptiles, the infiltration of the Golgi bodies has been described by D. R. Bhattacharya and K. B. Lal (1929), by P. R. Bhattacharya (1929), and Dutta and Asana (1928).

Das (1931) described the infiltration of the Golgi bodies from the follicular cells in three successive instalments in the pigeon. He also observed the infiltration of mitochondria.

In insects, the phenomenon has been observed by Ranade (1930) and by Shyam Mohan Srivastava and Bhattacharya (1935). The latter have also observed the infiltration of the mitochondria.

Ikeda reports the infiltration of the Golgi elements as well as of mitochondria from the follicular cells to the oocyte in birds (1928).

Thus the infiltration of the cytoplasmic inclusions from the egg membranes has been observed in a fairly wide range of animals, and the process is remarkably prominent.

In a recent paper Gosta Jägersten has questioned the reality of the infiltration. In his opinion the observations of Brambell and Ikeda are incorrect, for it is difficult to determine by the study of sections on which side of a membrane a certain particle lies. As for the infiltration of the Golgi elements through the zona radiata as depicted by Bhattacharya (1925), and Bhattacharya and collaborators (1929), he thinks that the ' dust-like ' particles are not Golgi bodies. Jägersten does not seem to have taken pains to study the subject in detail. The methods of infiltration vary in different animals, and can only be studied by the use of specific methods.

In *Calotes*, for example, fairly big lumps of Golgi elements pass from the follicle cells to the egg, through the zona radiata (Bhattacharya, Das, and Dutta, 1929). There is, however, hardly any reason to doubt that the infiltering particles are anything else than the Golgi bodies.

Jägersten's basic assumption is that the Golgi elements are always scaly in structure, which is hardly correct, for the apparatus appears to be polymorphic and assumes diverse shapes. Its morphology varies according to the nature of the cell in which it is found. The infiltering granules are strictly like the ones found in the follicular cells and there is hardly any justification for the statement that they do not represent the Golgi elements.

Nusbaum-Hilarowicz (1917) observed the infiltration of the mitochondria from the nurse cells to the oocyte in *Dytiscus* and a similar phenomenon was also reported by Govaerts in Hymenoptera (1933). Bhandari and Nath described the infiltration of Golgi bodies from the nutritive chamber to the egg along the nutritive strands in *Dysdercus cingulatus* (1930).

Srivastava (1934) reported the infiltration of Golgi bodies and mitochondria from the nurse-cells into the oocytes in *Musca* and a similar phenomenon has been observed in *Appias* by Shyam Mohan Srivastava and Bhattacharya (1935).

We have no doubt that the phenomenon of the infiltration of the formed cytoplasmic granules from the nurse-cells and the follicular cells to the egg is strictly comparable for both types of cells which normally function in order to contribute to the growth and development of the oocyte. While much of the material transmitted through these cells must be of non-living fluid and granular nature, the passage of the cell organelles can no longer be doubted. This becomes specially significant in view of the fact that the cytoplasmic inclusions have been held responsible for the production of the reserve food substances of the egg. Taking into consideration the nutritive function of the egg-membranes, as well as of the nurse-cells, the phenomenon of infiltration becomes easily understood, and can be expected to occur in all normal cases.

The object of writing this note is to lay emphasis on the fact that during the course of oogenesis the follicular cells contribute a definite quota of their cytoplasmic inclusions to the egg. This phenomenon has been observed in many classes of animals that have been investigated in this laboratory and there appears to be no doubt about the reality of the process and its nutritive function.

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ON PROPAGATION OF ELECTROMAGNETIC WAVES THROUGH THE ATMOSPHERE.

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(Read March 25, 1937.)

INTRODUCTION.

The subject of propagation of electromagnetic waves through the atmosphere is mostly treated in terms of the ray method. The present state of our knowledge is summarized in two excellent reports : (1) Report on the present state of our knowledge of the Ionosphere by S. K. Mitra published in the *Proceedings of the National Institute of Sciences of India*, Vol. I, No. 3, December 1935 ; hereafter referred to as Report 1 ; (2) Radio Exploration of the Upper Atmospheric Ionisation by E. V. Appleton in the *Reports on the Progress of Physics*, Vol. II, 1936 ; hereafter referred to as Report 2. Prof. Appleton remarks on page 133 of Report 2 :

' The discussion in the present section has so far been written in terms of a ray treatment. But it is well known that it is not possible adequately to describe optical phenomena in terms of geometrical optics when the refractive index μ varies appreciably within a wavelength in the medium in a direction normal to the wavelength. Now for total reflection at normal incidence, the wavelength becomes infinitely large as $\mu \to 0$, so that in this case the ray treatment needs further justification.'

The wave treatment of the problem has been tried by Hartree (1) in three important papers. In the first paper, he obtained, in the absence of the magnetic field, the differential equations for wave propagation and calculated the electric and magnetic fields. In the second, he derived an expression for μ, taking the earth's magnetic field into account. In the third paper, he obtained approximate expressions for the optical and equivalent paths for a stratified medium in which μ varies slowly. Reviewing the work of Hartree, Appleton says [Report 2, p. 133], ' On the whole, however, it may be said that the work of Hartree shows that the errors made in using a ray treatment are not serious in most practical problems '.

It is, however, not difficult to find illustrations which show the complete insufficiency of the ray treatment even for cases ordinarily met with : as an illustration, let us take the condition of reflection. A wave propagated vertically upwards is supposed to be reflected from the spot where the refractive index μ reaches the value 0, on account of increase in electron or ion concentration.

As Appleton has shown (see Report 1, p. 142, figs. 3-8, where q is plotted against electron-concentration, this criterion gives us the conditions of reflection

of the o-wave ($p^2 = p_0^2$), as well as of the x-wave ($p_0^2 = p^2 \pm pp_h$).   But μ can be zero, only if the collision frequency can be neglected.   In general, however, the collision frequency is never zero, and the refractive index is complex, of the form $q = \mu + i\chi$, where χ depends on the collision frequency and the ion-concentration and is not zero at any height excepting the lowest, so that q can never take a negative value even if the real part $\mu = 0$.   For example, see the q-curves drawn by M. Taylor (2) and Gobau (3).   They have shown that q takes up a steady, small, positive value with increasing values of ion-concentration, due to finite value of χ.   It may be mentioned, however, that according to the magneto-ionic theory, both μ and χ are functions of ion-concentration, and of the collision frequency ν, each of which again is a function of the height z.   None of the curves drawn either by Taylor or Gobau represents the actual variation of q with z.   For this purpose, the best course would be to make use of a three-dimensional representation with electron-concentration $\left(p_0^2 = \dfrac{4\pi Ne^2}{m} \right)$ along the x-axis, ν = collision frequency along the y-axis and q along the z-axis ; p^2 and ν are to be given all possible values, we get a surface representing q, and the actual (q, z) curve for the atmosphere is obtained by taking a section of this surface through points which represent the actual values of ν, and p_0^2 at a point z in the atmosphere.   This has not yet been attempted, but it can be shown that q can actually never become zero.   In the F-layer, there is probably some justification for neglecting collision as $\nu/p \simeq 10^{-3}$, but this cannot be said of the E-layer where $\nu/p \simeq 1$.

On account of these difficulties, several workers have tried to formulate other criteria for the reflection of waves.   Booker (4) says that appreciable reflection of an incident wave can take place only from such stratum, where either the variation of q per unit wavelength is considerable or $q \doteq 0$.   One of us (5) has shown that a better criterion for reflection is that group-velocity should be zero.   This criterion can, however, in the present state of our knowledge be used only when collisions can be neglected, for Rayleigh's theorem that group velocity $u = \dfrac{\delta\nu}{\delta k}$, where ν = frequency, k = wave number, holds only when the waves constituting a group are undamped.   We are not aware of any work which treats satisfactorily the case when the component waves are damped.   However, neglecting collisions, one of us, Rai (5), found that the criterion group-velocity $\mu = 0$ for reflections gives us the following four conditions for reflection :—

$$(\alpha) \quad p_0^2 = p^2 - pp_h \quad \ldots\ldots\ldots\ldots\ldots \quad x\text{-wave}$$

$$(\beta) \quad p_0^2 = p^2 \cdot \frac{p^2 - p_L^2}{p^2 - p_h^2} \quad \ldots\ldots\ldots\ldots \quad x\text{-wave}$$

$$(\gamma) \quad p_0^2 = p^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad o\text{-wave}$$

$$(\delta) \quad p_0^2 = p^2 + pp_h \quad \ldots\ldots\ldots\ldots\ldots \quad x\text{-wave}$$

$$\ldots \quad \ldots \quad (1)$$

Condition (β) is new and is not given by the hitherto assumed condition for reflection, *i.e.* $\mu = 0$. The actual existence of reflection (β) was detected at Allahabad by Pant and Bajpai (6), and, in fact, gave occasion for a revision of our ideas regarding the criterion for reflection.

The cases (α) to (δ) have been further discussed in a paper by Bajpai and K. B. Mathur (7). For the sake of illustration, we may work out from their paper the electron concentration required for the above four modes of reflection, taking $p = 23.3$ kilocycles, $f = \dfrac{23.3}{2\pi} = 3.70$, we find that

$$
\begin{array}{llll}
\text{Reflection } (\alpha) \text{ takes place when } N = & .88 \times 10^5/\text{cm}^3 \\
(\beta) \quad ,, \quad ,, \quad ,, \quad N = & 1.40 \times 10^5/\text{cm}^3 \\
(\gamma) \quad ,, \quad ,, \quad ,, \quad N = & 1.52 \times 10^5/\text{cm}^3 \\
(\delta) \quad ,, \quad ,, \quad ,, \quad N = & 2.40 \times 10^5/\text{cm}^3
\end{array} \qquad \cdots \qquad \cdots \quad (2)
$$

The question now arises how the same x-wave can get reflected from three different strata at one and the same time. If a wave is propagated vertically upwards, it gets split up into an o-wave, and an x-wave, which are propagated with different velocities in the ionosphere. On reaching the level where $N = .88 \times 10^5/\text{cm}^3$, the x-wave gets reflected. *But is this reflection complete or partial?* According to the ray treatment this should be complete, as the vanishing of group-velocity means that there is no further forward propagation of energy by the waves. But Pant and Bajpai (6) in this laboratory noticed the reflection of the x-wave according to the method (β), and Toshniwal (8) observed a threefold splitting of the wave, presumably of the x-wave, one of which he interpreted as mode (β). This observation was later verified by Leiv Harang (9) and recently all the four conditions of reflection have been verified by R. Jouaust and his co-workers. These cases show that reflection according to (α) is incomplete, even when we get the requisite electron-concentration, and the x-wave can sometimes leak through the layer, and get reflected under conditions which are still to be investigated, from the higher regions (β) and (δ). These cases therefore call for a revision of the treatment which has so far been pursued. But these are not the only cases which call for a revision of the ray treatment. Another is the existence of simultaneous reflection from layers at widely different heights. The best known example of this type is afforded by the case of the so-called sporadic E-layer reflection, also called Abnormal Region E-ionization by Appleton (for a detailed account, see Report 2, p. 159, where a reference to original papers will be found). It was first discovered in 1930 that ' echo-reflection often occurs from an atmospheric level approximately to that of region E for electric wave frequencies which are higher than the critical frequency for the normal region E '. Appleton concluded that ' either the recombination of ions is prevented or there is some ionizing agent present which can influence the dark side of the earth '.

The sporadic E-layer ionization has since been investigated by a large number of workers—Schafer and Goodal, Ranzi, Ratcliffe and White, Appleton

and Naismith (10)—with the object of finding out the conditions which give rise to the formation of the layer. It was first supposed that either thunderstorms or magnetic storms may give rise to a thin but concentrated layer of electrons at the E-height, but Kirby and Judson (11) have shown that the phenomenon cannot be due to extra-ionization produced by thunderstorms either occurring locally or within a radius of 300 Km., or due to magnetic storms. Berkner and Wells (12) have also confirmed this finding, and have further shown that sporadic E-reflection appears to be increasing in frequency as we proceed from the magnetic equator to the poles. This has been confirmed by L. Harang (13). Apparently, the sporadic layer is formed by some focussing action of the earth's magnetic field on the electrons at the E-layer. But we are not concerned in this paper with the causes giving rise to the sporadic E-layer but with the phenomenon that the same wave can get reflected from this layer, which is at the height of 100 Km., as well as from the much higher F-layer at one and the same instant (of course neglecting the time of transit).

The apparent explanation seems to be that a layer of electrical particles of abnormal density but extreme thinness is formed at the height of the normal E-layer. This layer reflects partly the energy of the waves, but part of the energy of the incident waves leaks through the layer, and gets reflected from the upper F_2-layer. This phenomenon cannot be understood if $\mu = 0$ is taken as the condition of reflection, for then reflection from the lower layer would be complete.

The M-reflections. Another phenomenon which points to the same conclusion is the existence of M-reflections investigated by Ratcliffe and White (14) and by Zenneck and Gobau. In this case the wave penetrates the E-layer, gets reflected from the F-layer, but the returned wave, instead of proceeding straight to the ground, gets reflected from the top of the E-layer, again gets reflected from the F-layer, and then proceeds straight to the ground. This phenomenon and the related E and F reflections show that the same wave can partly be reflected and can also leak through the same layer.

Let us see how all these phenomena can be explained.

§ 2.

For carrying out the programme sketched in §1, we have to start from the original Maxwellian equations, and derive equations for the propagation of electric and magnetic vectors associated with the electro-magnetic wave in the atmosphere, taking the effect of ion-concentration, collision and the earth's magnetic field into consideration. This has been done in a separate paper ; here only the results which will be necessary for the present discussion are quoted : We consider only vertical propagation (axis of z). Let (E_x, E_y), (H_x, H_y) denote the components of the electric and magnetic vectors associated with the signal. We further take the magnetic meridian as our plane of xz. Then it can be shown that the wave equations for their propagation are given by

$$\frac{dE_x}{dz} = -\frac{1}{c}\frac{dH_y}{dt}, \quad \frac{dE_y}{dz} = \frac{1}{c}\cdot\frac{dH_x}{dt}$$

$$\frac{dH_x}{dz} = \frac{iL}{c}\cdot\frac{dE_x}{dt} + \frac{K_2}{c}\cdot\frac{dE_y}{dt}$$

$$\frac{dH_y}{dz} = -\frac{K_1}{c}\frac{dE_x}{dt} - \frac{iL}{c}\cdot\frac{dE_y}{dt}$$

$$\left.\begin{array}{c}\\\\\\\\\\\\\end{array}\right\} \qquad \cdots \qquad \cdots \quad (3)$$

where K_1, K_2 are complex dielectric constants. L may be called mutual dielectric constant. Further, these quantities satisfy the equations

$$\frac{d^2E_x}{dz^2} = \frac{K_1}{c^2}\cdot\frac{d^2E_x}{dt^2} - \frac{iL}{c^2}\cdot\frac{d^2E_y}{dt^2}$$

$$\frac{d^2E_y}{dz^2} = \frac{iL}{c}\cdot\frac{d^2E_x}{dt^2} + \frac{K_2}{c^2}\cdot\frac{d^2E_y}{dt^2}$$

$$\frac{d^2H_x}{dz^2} = \frac{K_2}{c^2}\cdot\frac{d^2H_x}{dt^2} - \frac{iL}{c^2}\cdot\frac{d^2H_y}{dt^2}$$

$$\frac{d^2H_y}{dz^2} = \frac{iL}{c^2}\cdot\frac{d^2H_x}{dt^2} + \frac{K_1}{c^2}\cdot\frac{d^2H_y}{dt^2}$$

$$\left.\begin{array}{c}\\\\\\\\\\\\\\\\\end{array}\right\} \qquad \cdots \qquad \cdots \qquad \cdots \quad (4)$$

We can write out values of K_1, K_2, L in the general case by using the following notations, which as far as possible conform to those used by Appleton and Ratcliffe, and Mitra in their respective reports.

h ....Earth's magnetic field, components h_x, h_y, h_z.

p_h ....Larmor Frequency ....$\dfrac{eh}{mc}$.

p_x, p_y, p_z ....Components of Larmor Frequency.

p ....Pulsatance of the E.M. Wave.

$p_0{}^2 = \dfrac{4\pi N e^2}{m}$ ....Where N is the number of electrons or ions

per c.c. e, m are their charge and mass.

ν ....collision frequency for electrons or ions.   ·

$(\omega_x, \omega_y, \omega_z) = \dfrac{1}{p}(p_x, p_y, p_z)$, $\omega = $ resultant of $(\omega_x, \omega_y, \omega_z) = \dfrac{p_h}{p} = \dfrac{eh}{mcp}$.

$r = \dfrac{p_0{}^2}{p^2} = \dfrac{4\pi e^2}{mp^2}\cdot N$.

$\beta = 1 - \dfrac{i\nu}{p} = 1 - i\delta$, $\delta = \dfrac{\nu}{p}$.

$q = $ complex refractive index $= \mu + i\chi$.

We have in general when damping is not neglected

$$K_1 = 1 - r \cdot \frac{\beta^2 - r\beta - \omega_x^2}{C'}, \; K_2 = 1 - r \cdot \frac{\beta^2 - r\beta}{C'} \left.\vphantom{\frac{\beta}{C'}}\right\}$$
$$C' = \beta(\beta^2 - \omega^2) - r(\beta^2 - \omega_z^2), \; L = \frac{-r(\beta - r)\,\omega_z}{C'} \left.\vphantom{\frac{\beta}{C'}}\right\} \qquad \qquad (5)$$

The general solution of equations (3) and (4) is very much complicated and is not attempted here. We take the simplified case when collisions can be neglected, *i.e.* $\beta = 1$. In this case we have

$$K_1 = 1 - r \cdot \frac{1 - r - \omega_x^2}{(1 - \omega^2) - r(1 - \omega_z^2)}, \; K_2 = 1 - r \frac{1 - r}{(1 - \omega^2) - r(1 - \omega_z^2)}$$

$$L = -\frac{r(1 - r)\,\omega_z}{(1 - \omega^2) - r(1 - \omega_z^2)} \qquad \qquad \dots \qquad \dots \qquad (6)$$

For the solutions of equations (3) and (4), we may first utilize the facts that every quantity E or H is proportional to exp. (ipt)—then bearing in mind that E_x, E_y are now only functions of z, and introducing a new variable $u = \dfrac{zp}{c}$, we have

$$\frac{dE_x}{du} = -iH_y, \quad \frac{dE_y}{du} = iH_x,$$

$$\frac{dH_x}{du} = -LE_x + iK_2E_y; \quad \frac{dH_y}{du} = -iK_1E_x - LE_y$$

$$\frac{d^2E_x}{du^2} = -K_1E_x + iLE_y; \quad \frac{d^2E_y}{du^2} = -iLE_x - K_2E_y \left.\vphantom{\frac{d}{d}}\right\} \qquad \dots \qquad (7)$$

$$\frac{d^2H_x}{du^2} = -K_2E_x - iLE_y; \quad \frac{d^2H_y}{du^2} = iLH_x - K_1H_y$$

[The last two equations in H_x, H_y are strictly not quite rigorous].

In the solution of these equations, we may as a first step regard the quantities K and L as constants, *i.e.* not varying with z, and then we get all the results deduced by Appleton and others regarding splitting of the waves into o and x-components, their polarization, refractive indices, and the conditions for reflection [conditions (α), (γ), (δ)]. When the expressions (5) are utilized, the usual expressions for refractive index, and absorption coefficient of the two components can also be deduced.

But a little reflection shows that this procedure is not strictly justified, for K and L, both involve r and ν (ionization and collision frequency) and these vary with height. We are therefore, in general, not justified in proceeding with the solution on the assumption that K and L are constants.

To illustrate this point, let us take the simplest possible case, *viz.* that of propagation in the magnetic equator. We have then $\omega_z = 0$, $\omega_x = \omega$. We have therefore

$$K_1 = 1 - r, \; K_2 = 1 - \frac{r(1 - r)}{(1 - r) - \omega^2}, \; L = 0 \qquad \dots \qquad \dots \qquad (8)$$

The equations reduce to :

$$o\text{-wave} : \frac{d^2 E_z}{du^2} + (1-r)E_z = 0 \qquad \frac{d^2 H_y}{du^2} + (1-r)H_y = 0$$

$$x\text{-wave} : \frac{d^2 E_y}{du^2} + \left\{ 1 - \frac{r(1-r)}{(1-r)-\omega^2} \right\} E_y = 0 \qquad\qquad \qquad (9)$$

$$\frac{d^2 H_x}{du^2} + \left\{ 1 - \frac{r(1-r)}{(1-r)-\omega^2} \right\} H_x = 0$$

For the o-wave, it is usual to take $1 - \dfrac{p_0^2}{p^2}$ as equal to μ^2, and the vanishing of this gives us the condition for reflection of the o-wave : $viz.\ p_0^2 = p^2$; similarly we may take $\mu_x^2 = 1 - \dfrac{r(1-r)}{(1-r)-w_x^2}$ and this vanishes when $p_0^2 = p^2 \pm pp_h$. But since r is a function of z, the procedure is not justified. We cannot, in fact, talk of a refractive index in the usual sense. These equations are of the form

$$\frac{d^2\phi}{du^2} + k^2\phi = 0 \qquad .. \qquad .. \qquad .. \qquad .. \qquad (10)$$

where k^2 is not a constant, but a function of (u).

Equations of this type were first discussed by Lord Rayleigh (15) ; see ' On the propagation of waves through a stratified medium with special reference to the question of reflection '. The following treatment is based on Lord Rayleigh's with the necessary modification. The same treatment was later given by Gans (16), apparently without a knowledge of Rayleigh's previous work. It may also be mentioned that Gamow (17) has used the same method in his famous work on the ' Penetration of the Potential Barrier of Nuclei of Atoms by high energy particles '.

Let us put $\phi = e^{s(u)}$. We have then

$$\frac{d\phi}{du} = \phi \frac{ds}{du}, \ \frac{d^2\phi}{du^2} = \left\{ \frac{d^2 s}{du^2} + \left(\frac{ds}{du}\right)^2 \right\} \phi \qquad .. \qquad .. \qquad (11)$$

The differential equation (10) takes the form

$$\frac{d^2 s}{du^2} + \left(\frac{ds}{du}\right)^2 + k^2 = 0 \qquad .. \qquad .. \qquad .. \qquad (12)$$

If it is possible to neglect the first term with respect to the second, $i.e.$ if

$$\left| \frac{\dfrac{d^2 s}{du^2}}{\left(\dfrac{ds}{du}\right)^2} \right| = \left| \frac{d}{du} \cdot \frac{1}{\dfrac{ds}{du}} \right| \ll | \ , \text{ we have}$$

$$\left(\frac{ds_1}{du}\right)^2 + k^2 = 0 \qquad .. \qquad .. \qquad .. \qquad .. \qquad (13)$$

Here s_1 denotes the first approximation to s. We have then

$$\frac{ds_1}{du} = \pm ik, \text{ or } \pm l$$

and $\quad \phi = C \exp. \left[\pm i \int_{u_1}^{u_2} k\, du \right], \text{ or } C \exp. \left[\pm \int_{u_1}^{u_2} l\, du \right] \qquad .. \quad (14)$

The second form holds when k^2 is negative $= -l^2$.

Let us now work out a second approximation. We now regard C as varying with u or z. It can be easily shown that C satisfies the equation

$$\frac{d^2C}{du^2} + 2ik \frac{dC}{du} + ik'C = 0 \qquad .. \qquad .. \qquad .. \quad (15)$$

where $k' = \dfrac{dk}{du}$.

If we suppose that $\dfrac{d^2C}{du^2}$ can be neglected, we easily obtain from (15)

$$C = \frac{A}{\sqrt{k}} \quad \text{or} \quad \frac{A'}{\sqrt{l}},$$

according as k^2 is positive or negative.

So the second approximation gives us, as the solution of (10)

$$\phi = \frac{A}{\sqrt{k}}\, e^{\pm i \int k\, ds} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \quad (16A)$$

$$\text{or} \quad \frac{A'}{\sqrt{l}} . e^{\pm \int l\, ds} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \quad (16B)$$

This solution can be regarded as correct if

$$\frac{d^2}{dz^2} \left(k^{-\frac{1}{2}} \right) = 0 \qquad .. \qquad .. \qquad .. \qquad .. \quad (17)$$

We shall assume that this condition is satisfied, though actually, as can easily be seen this is strictly not the case even approximately. Let us now see how these solutions can be applied to the present case. As the wave moves up in the atmosphere, $r = \dfrac{4\pi e^2}{mp^2} . N$ gradually approaches the value 1, and ultimately may exceed 1, so that $k^2 = 1 - r$ becomes negative. The actual state of affairs is represented in Fig. 1. Here the abscissa 'z' represents height, the ordinate $r = \dfrac{4\pi e^2}{mp^2} . N$ is proportional to the electron-concentration. The distribution of electrons is represented by the curve $OPQR$ which is of course fancied. If wave of some other frequency were employed, the position of the line $r = 1(A, A_1, A_2, A_3)$ would shift with respect to the curve, e.g. for $p_1 > p$ the line would go up, and ultimately may cross over the crest of the curve $OPQR$. For $p_2 < p$ the line AA_1A_2 would move
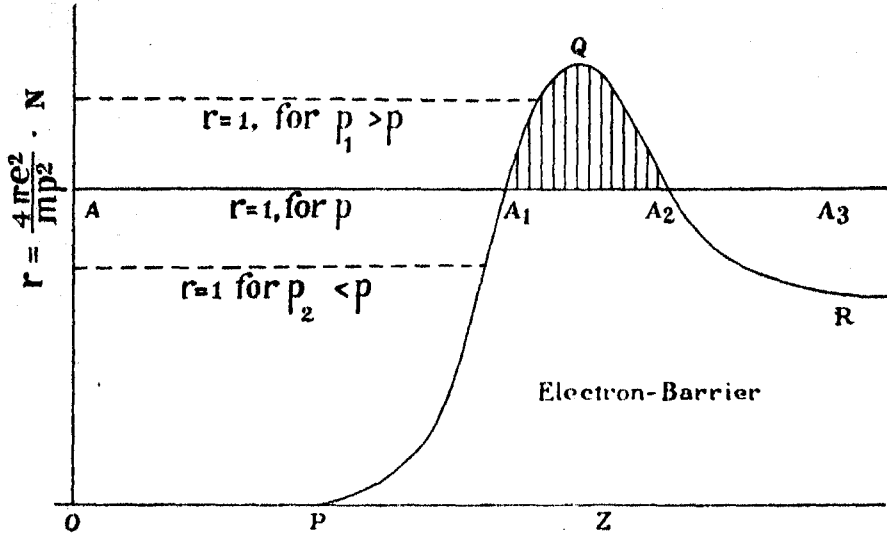
Fig. 1.

down as shown in Fig. 1. From A to A_1, the value of $k^2 = 1 - r$ is positive, at A_1 it becomes zero, between A_1 and A_2 it is negative, and then it is again positive. We have to write different suitable solutions of (10) for the three different regions, and apply the conditions of continuity $\left(\text{equality of } \phi \text{ and } \dfrac{d\phi}{du}\right)$ at the transition points A_1 and A_2. Then it can be easily shown that there is a forward and backward wave of type (16A) in the region between O and A_1, in the region A_1A_2, the disturbance is damped (16B) and there are two components, beyond A_2 there is only one wave (16A) with the negative sign. The coefficient of transmission through the barrier is given by

$$T = 4 \left(\frac{1-r_1}{1-r_3}\right)^{\frac{1}{4}} e^{-\int_{u_1}^{u_2} \sqrt{1-r} \cdot du} \qquad .. \qquad .. \qquad .. \ (18)$$

where r_1 is the limiting value of r in the region (OA_1), r_2 in the region A_2. u_1, u_2 are the co-ordinates for the points A_1, A_2 respectively. We have, restoring the old co-ordinates

$$T = 4 \left(\frac{p^2}{p^2 - p_{02}^2}\right)^{\frac{1}{4}} \exp\cdot\left[-\frac{1}{c}\int \sqrt{p_0^2 - p^2} \cdot dz\right]_{z_1}^{z_2} \qquad .. \qquad .. \ (19)$$

We shall try to calculate its value in some representative cases. In the equation (19), $p_0^2 = \dfrac{4\pi e^2}{m} \cdot N$, where N is the actual electron-concentration at a height z within A_1A_2. As 'p' is fixed, we can put $\dfrac{4\pi e^2}{mp^2} = N_1$, so N is

the electron-concentration at the layer where reflection takes place. Hence the index of e in (19) is given in the case of electrons by

$$-\frac{1}{c}\left(\sqrt{\frac{4\pi e^2}{m}}\right)\int_{z_1}^{z_2}\sqrt{N_0-N_1}\cdot dz = -1\cdot9\times10^{-6}\cdot\int_{z_1}^{z_2}\sqrt{N-N_1}\,dz \quad .. \quad (20)$$

and m refers to electrons. If they refer to ions, we have

$$\text{the index} = -8\cdot3\times10^{-9}\int_{z_1}^{z_2}\sqrt{N-N_1}\,dz \quad .. \quad .. \quad (21)$$

The value of the integral cannot be obtained unless we know the form of the electron-concentration curve above the line $r = 1$. Let us suppose that it is in the form of an isosceles triangle, so that for the rising half,

$$N = N_1+\alpha(z-z_1)$$

then the value of N at the peak will be N_m. Then the half-breadth of the barrier $= \dfrac{Nm-N_1}{\alpha}$. For the descending half, $N = N_m-\alpha z$. We must have some idea of the values of N_1, N_2, α and the half-breadth in order to be able to make some calculations.

It is well known, however, that for the E-layer, α is large, and the thickness of the layer is small, while for the F-layer, α is small, and the thickness of the layer is large. But as figures are available only for the F-layer, we shall give a calculation based on data for F alone.

In a case cited by Appleton, the values of N are given as follows :—

Penetration Frequency for $(h = 300$ Km.$) = 4$ megacycles, $N = 1\cdot98\times10^5$

$(h = 210$ Km.$) = 3\cdot7$,, $N = 1\cdot70\times10^5$

So we have $\dfrac{dN}{dz} = \dfrac{2\cdot8\times10^4}{90\times10^5} = 3.10^{-3}$ electrons per cm.

Using these values we have

$$\text{the index} = -1\cdot90\times10^{-6}\ \alpha^{\frac{1}{2}}\,b^{\frac{3}{2}}\cdot\frac{4}{3}$$

where $b =$ half-breadth of the barrier.

Taking into account the factor $\left(\dfrac{p^2}{p^2-p_0{}^2}\right)^{\frac{1}{4}}$, we find that the amount of energy transmitted falls to half of its value, for a barrier of the form shown in fig. 1, and for gradient and electron density characteristic of the F-layer, if the half-breadth of the layer is about $1\cdot5$ Km. This calculation is of course fancied, but it shows that the wave can penetrate some thicknesses of the ionized layer without appreciable diminution in intensity. For the E-layer, α is larger, but b is smaller, hence if the thickness of the layer is of the order of a kilometer a part of the energy of the incident wave may be transmitted, though the value of μ is zero for the wave transmitted at the point where it meets the electron-barrier.

This treatment of penetration of electron or ion-barriers by e.m. waves cannot be utilized for the x-wave, which has singularities at

$$(\alpha)\ p_0{}^2 = p^2 - pp_h, \quad (\beta)\ p_0{}^2 = p^2 \cdot \frac{p^2 - p_l{}^2}{p^2 - p_h{}^2}, \quad \text{and}\ (\delta)\ p_0{}^2 = p^2 + pp_h.$$

The problem is still under consideration.

In conclusion, we wish to express our thanks to Dr. G. R. Toshniwal for many useful discussions and to Mr. K. B. Mathur and Dr. Rakshit for much help in the calculations.

SUMMARY.

In this paper, the ray treatment of passage of e.m. waves through the ionosphere has been critically reviewed, and a wave treatment has been given for the o-wave for propagation in the magnetic equator. It has been shown that contrary to the implicit assumption in the ray treatment which requires complete reflection at the point in the ion-barrier where μ falls to zero, there may be considerable penetration by the wave of the barrier, even when the thickness of the barrier amounts to several kilometers.

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CHEMICAL EXAMINATION OF *INDIGOFERA ENNEAPHYLLA,* LINN. AND THE ISOLATION OF ITS ACTIVE PRINCIPLE.

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(Read March 25, 1937.)

Indigofera enneaphylla, Linn. is a common annual or perennial herb belonging to the Natural Order—Leguminosæ. It is distributed throughout India, Burma, the Malaya Peninsula and Northern Australia and particularly in Bengal. The Sanskrit, Bengali and Hindi name of the plant is *Vasuka.* It is regarded by Indian medical practitioners as alterative in old venereal affections. The juice of this plant is used as an antiscorbutic and diuretic. According to Ainsle and Mudan Sheriff the plant has several other medicinal properties. No work of a chemical nature has yet been done on this plant, in spite of the fact that it is so abundant everywhere, particularly after the rainy season.

The plant on extraction with alcohol and subsequent working up of the alcoholic extract in accordance with the experimental part, gave its active principle in the form of two unsaturated hydrocarbons which have been named 'Indigoferin' and 'Enneaphyllin'. It may be mentioned that never before has any hydrocarbon been isolated from any plant belonging to the family of Leguminosæ.

EXPERIMENTAL.

Forty kilograms of the entire plant were collected locally and dried in the sun. The fresh plant lost 43·2% of moisture during the process of drying. On complete incineration it yielded 15·27% of a grey coloured ash, 39% of which was water-soluble. The following radicals were detected :—

(*a*) In the water-soluble portion :—

K, SO_4, and Cl.

(*b*) In the water insoluble portion :—

Al, Fe (in traces), Ca, Mg . CO_3.

Of the total ash 9% consisted of matter which was insoluble in a mixture of nitric and hydrochloric acids. This was found to be mainly silica.

In order to have an idea about the extractives present in the plant, ten grams of the dried and ground stuff were exhaustively extracted with the following solvents in succession with the results given below :—

Ethyl alcohol.—By this solvent 7·21% of extract was obtained. The colour of the extract was deep green and it was somewhat sticky and possessed a peculiar odour.

Methyl alcohol.—This gave 6·12% of extract which was much less sticky than that obtained with ethyl alcohol but possessed almost a similar odour.

Acetone.—This gave 1·31% of extract which was dry and yellowish-green and possessed a faint odour.

Benzene.—7·38% of a thick viscid dark green extract was obtained which possessed a strong odour.

Chloroform.—This gave 5·15% of extract which was light green and dry, and possessed a faint odour.

Carbon tetrachloride.—By this was obtained 5·56% of extract which possessed a dry and yellowish-green appearance and a faint smell.

Water.—4·65% of a viscid green extract was obtained which had an unpleasant smell.

The active principle of the plant has been obtained as a mixture of two unsaturated hydrocarbons of high molecular weights. One of them is soluble in hot acetone from which it comes down on cooling. This has been named Indigoferin. The other is insoluble both in hot and in cold acetone. This has been named Enneaphyllin. The fact that one is soluble in acetone and the other is not has been utilized in separating them from each other. The formula of Indigoferin is $C_{70}H_{140}$ and of Enneaphyllin $C_{90}H_{154}$.

The details about the isolation and examination of the active principle of the plant are given below.

One kilogram of the dried and ground plant was introduced into a flask and refluxed with 90% alcohol on a water-bath for six hours. The extraction flask was then quickly removed from the water-bath and the alcohol was filtered hot. It was allowed to cool when a solid precipitate appeared in the alcohol. The whole substance was allowed to stand overnight. The next day the alcohol was filtered off and the solid substance thus separated. The latter was given twelve to fifteen washings with cold alcohol in order to wash off the chlorophyll which gave a deep green colour to the precipitate. By this means the solid gradually lost the green colour becoming ultimately white. A large number of extractions with the fresh plant were done in a similar way. The solid extracts were allowed to dry in the sun. The yields of the dried solid extract thus obtained varied from ·15 to ·2%.

The alcoholic mother liquor obtained after separating the solid precipitate was concentrated to a fourth of the original bulk by distilling off the rest of the alcohol. On cooling the concentrated liquid, a solid precipitate appeared in it. The amount of solid thus obtained was very small. It was filtered off from the alcohol and the adhering green colour of chlorophyll was removed by washing with cold alcohol. The white solid thus obtained was found on examination to be the same substance which separated from the hot alcoholic extract of the plant when it was allowed to cool.

The concentrated alcoholic mother liquor obtained, after removal of the solid precipitate, was tested for the presence of glucosides, but the tests

employed revealed that none was present. The concentrated mother liquor was also tested for the presence of alkaloids but no alkaloid could be detected.

The solid alcoholic extracts were dissolved by warming in water-free benzene and the benzene solution filtered in order to separate any inorganic matter which might have been present in the alcoholic extract and which did not dissolve in benzene. The benzene solution was concentrated to a small bulk and the solid was recovered from it by evaporating off the rest of the benzene in the sun. The substance which did not dissolve in benzene was found on examination to be potassium sulphate.

Examination of the solubility of the solid plant extract in different solvents revealed the fact that it is a mixture of two substances, A and B, of which the component A is soluble in hot acetone (from which it comes down on cooling), while B is insoluble either in the hot or in the cold solvent. By taking advantage of this fact the mixture was separated into the two components, A and B, by boiling the mixture in acetone and then filtering the acetone through a hot water funnel. The proportions of A and B in the mixture was found to be about 3 to 1. The component A has been named Indigoferin and the component B Enneaphyllin.

EXAMINATION OF INDIGOFERIN.

Indigoferin was crystallized from acetone by dissolving it in hot acetone and allowing the solution to cool when very small needle-shaped crystals, visible under the high power of the microscope, separated. The solid was repeatedly crystallized from acetone in the manner stated until the last traces of xanthophyll, which gave a yellowish tinge to the white solid, were completely removed. To remove the last traces of colouring matter from the solid, the latter had to be crystallized from acetone nearly ten to twelve times. The purified solid was white in colour and melted at 77°C.

The solubilities of the substance in various solvents are given below :

Ethyl alcohol, ethyl acetate, pyridine.—Slightly soluble in the hot solvents, getting precipitated on cooling.

Methyl alcohol and acetone.—Soluble in hot, and crystallizes on cooling, in a needle-shaped form.

Benzene, toluene and xylene.—Easily soluble in hot and does not get precipitated on cooling.

Chloroform, carbon tetrachloride and glacial acetic acid.—Fairly soluble in hot, getting partially precipitated on cooling.

Petrol ether, ether and carbon disulphide.—Very sparingly soluble in the boiling solvents.

Naphthalene.—Dissolves in molten naphthalene.

Water.—Insoluble.

The following combustion results show that the substance is a hydrocarbon :
$$C = 84 \cdot 85\%, \ H = 14 \cdot 61\%.$$

The empirical formula of the compound as calculated from these combustion results comes to be CH_2.

The molecular weight of the compound as determined by Rast's camphor method gave the following values :

    1. 962.

    2. 979.

    3. 1004.

The formula $C_{70}H_{140}$ requires the molecular weight of the compound to be 980.

The compound was found to be unsaturated since it absorbed bromine from a solution of the latter in carbon tetrachloride. The unsaturation was estimated by determining the Iodine Value of the compound by means of Wiji's solution.

The Iodine Value obtained experimentally was 24·80. Assuming that two atoms of iodine are taken up by one molecule of the substance, the theoretical Iodine Value expected is 25·90. From these data it is obvious that the compound has a single double bond in its molecule.

The compound on burning gives out a characteristic smell which resembles that of a burning candle. This fact suggests that the compound is probably an aliphatic compound resembling paraffin wax.

DIBROMO DERIVATIVE.

The dibromo derivative was prepared by dissolving the substance in carbon tetrachloride and adding to it a slight excess of bromine in carbon tetrachloride solution, refluxing the whole thing on a water-bath for two hours, separating the carbon tetrachloride solution of the dibromo derivative after removing the excess of bromine by an aqueous solution of sodium thiosulphate, and finally distilling off the carbon tetrachloride. The dibromo derivative melted at 81°C. Its solubility was studied in the following solvents :—

    Benzene, ethyl alcohol and methyl alcohol.—Soluble in hot.

    Chloroform and carbon tetrachloride.—Soluble.

    Acetone and water.—Insoluble.

The percentage of bromine estimated in the bromo derivative is 14·131%. Assuming that two atoms of bromine are taken up by Indigoferin, the theoretical percentage of bromine is 14·035%. Hence the formula of the dibromo derivative is $C_{70}H_{140}Br_2$.

The fact that one double bond is present in the molecule of Indigoferin is corroborated from the result of the estimation of bromine in the bromo derivative.

Indigoferin was found to be optically inactive which may be due to the fact that it may be racemic.

EXAMINATION OF ENNEAPHYLLIN.

After the separation of Indigoferin from the solid alcoholic extract by repeated treatment with acetone, the remainder was placed in a soxhlet and exhaustively extracted with acetone for 30 hours in order to remove the last traces of Indigoferin from it. The solid, Enneaphyllin, was then dissolved in nitrobenzene at the temperature of the water-bath when a solution of the solid was obtained in nitrobenzene. On cooling the nitrobenzene solution, the solid separated and it was filtered off and the residue washed repeatedly with petrol ether until the smell of nitrobenzene was completely removed. After repeating the whole process once more the solid was dried in vacuo over fused calcium chloride and finally crystallized from benzene. The crystals were rod-shaped and were visible under the high power of the microscope. The dried solid was light brown in colour and melted at 98°C.

The following are the results of the solubility of the substance in various solvents :—

Ethyl alcohol, methyl alcohol and ethyl acetate.—Soluble in hot solvents but comes down on cooling.

Petrol ether, ether and carbon disulphide.—Very sparingly soluble in the boiling solvents.

Chloroform and carbon tetrachloride.—Fairly soluble in hot but gets precipitated on cooling.

Benzene, toluene and xylene.—Dissolves easily on warming and does not get precipitated on cooling.

Acetone, pyridine, glacial acetic acid and water.—Insoluble.

Naphthalene.—Dissolves in molten naphthalene.

The following combustion results show that the substance is a hydrocarbon :—

$$C = 87 \cdot 1\%, \ H = 12 \cdot 38\%.$$

The empirical formula of the compound as calculated from these combustion results comes to be $C_{10}H_{17}$.

The molecular weight of the compound as determined by Rast's camphor method gave the following values :—

1. 1216.
2. 1230.

The formula $(C_{10}H_{17})_9$ or $C_{90}H_{153}$ requires the molecular weight to be 1234.

The compound was found to be unsaturated since it absorbed bromine from a solution of the latter in carbon tetrachloride. The unsaturation was estimated by determining the Iodine Value of the compound by means of Wiji's solution.

The Iodine Value obtained experimentally is 22·44. Assuming that two atoms of iodine are taken up by one molecule of the substance, the theoretical

Iodine Value expected is 20·58. From these data it is evident that the compound has a single double bond in its molecule.

DIBROMO DERIVATIVE.

The dibromo derivative of Enneaphyllin was prepared in exactly the same way in which that of Indigoferin was prepared. Its solubility was studied in the following solvents :—

Benzene.—Fairly soluble in hot but comes down on cooling.

Ethyl and methyl alcohols.—Slightly soluble in hot.

Carbon tetrachloride and chloroform.—Soluble.

Acetone and water.—Insoluble.

The dibromo derivative melted at 88°C.

The percentage of bromine estimated in the bromo derivative is 11·392%. Assuming that two atoms of bromine are taken up by Enneaphyllin, the theoretical percentage of bromine is 11·477%. Hence the formula of the dibromo derivative is $C_{90}H_{154}Br_2$.

The fact that one double bond is present in the molecule of Enneaphyllin is corroborated from the result of the estimation of bromine in the bromo derivative.

Enneaphyllin was found to be optically inactive which may be due to the fact that it may be racemic.

Had Enneaphyllin been a straight chain compound 14 (fourteen) double bonds should have existed in its molecule. But the fact that there is only a double bond in the molecule shows that the compound is probably a cyclic one with a complex molecular structure.

COLOUR AND CHEMICAL CONSTITUTION OF ISO-NITROSO-THIO-BARBITURIC ACID AND ITS INORGANIC AND ORGANIC SALTS.

By RATAN LAL *and* SIKHIBHUSHAN DUTT, *Chemical Laboratory, Allahabad University.*

(*Read March 25, 1937.*)

Malonyl urea or barbituric acid on treatment with nitrous acid yields violuric acid. In a similar manner if thio-barbituric acid is treated with nitrous acid, the compound formed should be iso-nitroso-thio-barbituric acid, which may on analogy be called thiovioluric acid.

THIO-BARBITURIC ACID. ISO-NITROSO-THIO-BARBITURIC ACID OR THIOVIOLURIC ACID.
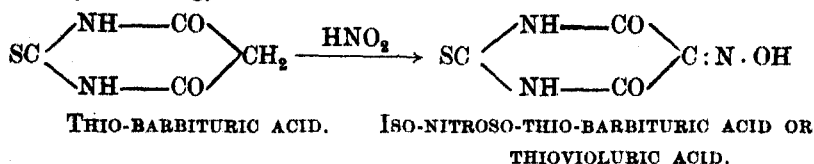
Since the violurates are all coloured compounds it is naturally expected that the salts of thiovioluric acid should yield even more interesting results. Though much work has been done on violuric acid and violurates from the point of view of colour and their chemical constitution the corresponding sulphur compounds, viz. the thioviolurates are quite unknown. Consequently *iso-nitroso-thio-barbituric* acid was prepared *in a workable* quantity and a large number of its salts, both organic and inorganic, were obtained. They proved to be highly coloured compounds yielding fluorescent purple violet solutions. The present paper, therefore, is an attempt to study the phenomenon of colour in these compounds and its relation to their chemical constitution.

The thioviolurates derived from very weak organic bases like aniline, some of which have a basicity constant of the order of 10^{-5}, have very intense colours, giving absorption bands between 5,900–6,025 Å, and they are in no way less intense than the alkali violurates. It is evident therefore that even the high basic nature of the base is not very essential to produce the colour phenomenon, though it may intensify the colour to some extent.

Thiovioluric acid has been found to have a dissociation constant $K = 6.73 \times 10^{-5}$. In aqueous solution containing one gram molecule of the acid in 128 litres of water about 8% of molecules are present, dissociated into ions. Such a solution has a very faint yellow colour. The colour of the sodium salt however at this dilution is intense purple, the degree of dissociation being 0.729, i.e. about 73% of the molecules exist as ions. This intensification in colour may therefore be attributed to the greater dissociation of the salt into ions

than the original acid. But the work of Magnaninni (*Gazetta*, 1894, *24*, I, 48), Hantzsch (*Ber.*, *42*, 966 [1902]) and Guinchard (*Ber.*, *32*, 1723 [1899]) on the salts of violuric acid has definitely proved that the colour phenomenon in alkali violurates and other oximido compounds like violuric acid is not due to electrolytic dissociation of the molecules into ions. The same holds good for thiovioluric acid and its salts.

All these facts go to show that the colour of thioviolurates is neither intimately connected with electrolytic dissociation nor with the strength of the base and therefore the true solution of the problem must be sought elsewhere.

It has been shown by one of the present authors (Dutt, *J.*, 1926, *129*, 1171 ; *J. Indian Chem. Soc.*, 1927, *4*, 99) that in a union between two atoms by a double bond the valency directions of the original atoms tend to straighten out and produce a great strain in the molecule, depending upon the amount of distortion suffered by the valency directions of the original atoms. The greater the strain in the molecule the more highly coloured is the compound. In a double bond between oxygen and nitrogen the amount of distortion suffered by the valency directions on theoretical considerations is 300°. Consequently it is the most highly strained system of all other combinations. The idea is clearly manifested in the remarkable instability of these compounds. The true nitroso compounds often decompose on the slightest provocation. They are easily attacked by reducing and oxidising agents with the formation of less strained amino and nitro compounds. This high strain in the molecule of nitroso compounds is responsible for colour and makes them highly absorptive.

Due to the high strain in the molecule many of the nitroso compounds tend to lose their internal strain by formation of ring compounds thus

$$2 \text{ —N}\!=\!\text{O} \longrightarrow \begin{array}{c} \text{—N}\text{——}\text{O} \\ | \quad | \\ \text{O}\text{——}\text{N—} \end{array}$$
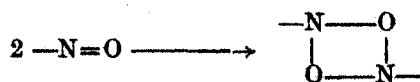
and in the latter form they are colourless. But if the nitroso group is in a molecule containing a labile hydrogen atom it automatically rearranges itself into a condition of less strain in the following manner, forming the iso-nitroso derivative

$$\text{—N}\!=\!\text{O} \xrightarrow{\text{H}} \text{=N—O}\cdot\text{H.}$$
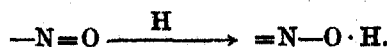
A similar thing happens with iso-nitroso-thio-barbituric acid. Since it behaves as a weak monobasic acid, it may be represented by the formula (1) shown below, in which the H atom marked with an asterisk is replaceable by metals. This is known as the oximino ketonic form.

$$(1) \quad \text{SC} \underset{\text{NH}\text{——}\text{CO}}{\overset{\text{NH}\text{——}\text{CO}}{\bigg\langle}} \text{C}\!=\!\text{N}\cdot\text{OH *} \quad \text{Oximino Ketonic form.}$$
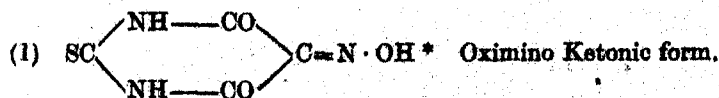
But an alternative structure can be formed due to the tautomerization of the marked H atom to give the 'Nitroso Enolic' formula (2) which is equally capable of existence.

$$(2) \quad SC \begin{array}{c} NH\!-\!\!-\!C\!-\!OH \\ \diagup \qquad\qquad \diagdown \\ \diagdown \qquad\qquad \diagup \\ NH\!-\!\!-\!CO \end{array} C\!-\!N\!=\!O \quad \text{Nitroso Enolic form.}$$
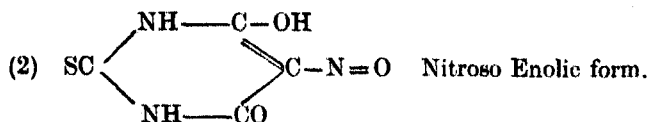
This contains the highly strained grounding—N = O and hence, according to the theory of Dutt (*loc. cit.*), it must be a highly coloured substance. On the other hand, if the oximino ketonic formula be correct, the thiovioluric acid should not have any colour at all or only a pale yellow colour. Iso-nitroso-thio-barbituric acid or thiovioluric acid, though bright yellow in the solid state, gives only a faint yellow solution with absorption at 4403 Å. It is therefore evident that it has a structure tautomeric between the oximino ketonic and nitroso enolic form.

$$SC \begin{array}{c} NH\!-\!\!-\!CO \\ \diagup \qquad\qquad \diagdown \\ \diagdown \qquad\qquad \diagup \\ NH\!-\!\!-\!CO \end{array} C\!=\!N\cdot OH \quad \xleftarrow{\quad} \quad \xrightarrow{\quad} \quad SC \begin{array}{c} NH\!-\!\!-\!C\cdot OH \\ \diagup \qquad\qquad \diagdown \\ \diagdown \qquad\qquad \diagup \\ NH\!-\!\!-\!CO \end{array} C\!-\!N\!=\!O$$

Oximino Ketonic.
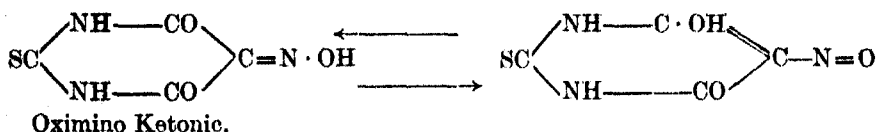
Thus when thiovioluric acid is put in solution the less strained configuration (1) must tend to pass into the highly strained structure (2), due to the lightness of the hydrogen atom and the consequent ease with which it can be transferred from one position to another, this tautomerism between the two forms is sufficiently rapid and the development of full colour, as is expected from the structure (2), is not manifested. Hence it can be concluded that in solution thiovioluric acid mainly exists in the form (1), very little of (2) being present.

The state of affairs becomes considerably modified when a salt of thiovioluric acid is examined instead of the acid itself. Under such circumstances, due to the greater load of the substituent metal or the basic radical, the tautomerism between the two forms is not so easy and the more highly strained configuration (2) results wherever its existence is possible.

The —CO— group in the molecule is really the residue of a carboxyl and still retains its carboxylic character in a modified form, due to the presence of —NH— group in its neighbourhood, whose basic character it has more than neutralised. When such a group enolises by the transference of the labile H atom it becomes much more acidic than an —N.OH group. It can be easily seen therefore that to neutralize an alkali like sodium hydroxide the original weakly acidic oximino ketonic form has to tautomerise into the more acidic nitroso enolic structure. But once the hydrogen atom has been substituted in the latter position it becomes fixed, due to salt formation, and, due to the heavy load, cannot tautomerise to the less strained oximino ketonic form. It is due to this that a highly strained structure results which is in

fact responsible for the intense colour of the thioviolurates and makes them so highly absorptive.

Having studied the effect of nitrogen on colour it would not be without interest to see how the replacement of an oxygen atom by sulphur in violuric acid and violurates modifies their colour.
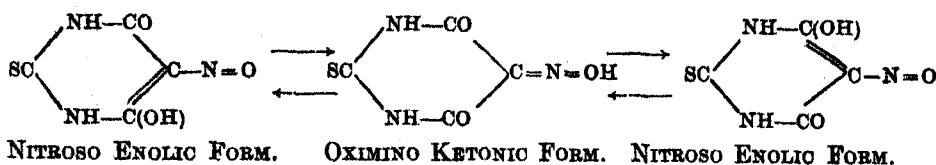
It has been proved by Dutt (loc. cit.) that an unsaturated group $= C = S$ shifts the position of the absorption maximum in organic compounds towards the region of wavelength longer than that corresponding to the group $= C = O$. Though, like oxygen, sulphur is divalent and potentially quadrivalent it has much greater atomic weight and consequently its loading effect is more intense. This has further been confirmed by the researches of Reid (J. Amer. Chem. Soc., 1926, 46, 1936 ; 1926, 48, 528) and of Dutt and Watson (J., 1922, 121, 1939, 2414) on sulphur substituted dyes. They have regarded the group $= C = S$ as a more powerful chromophore than the corresponding group $= C = O$. A very interesting verification of such a phenomenon can be made from a study of the absorption spectra of thioviolurates and their comparison with the corresponding violurates prepared by Ghatak and Dutt (J. Indian Chem. Soc., 1928, 5, 665). The table given below shows that in all cases the wavelength corresponding to maximum absorption is longer in thioviolurates than in the corresponding violurates.

TABLE 1.

No.	Salt with	Absorption Maxima of ' Violurates ' at N/128 dilution.	Absorption Maxima of ' Thioviolurates ' at N/128 dilution.
1	Ammonium Hydroxide	5832 Å	5837 Å
2	Methylamine	5782 ,,	5892 ,,
3	Dimethylamine	5793 ,,	5858 ,,
4	Trimethylamine	5712 ,,	5820 ,,
5	Ethylamine	5697 ,,	5870 ,,
6	Diethylamine	5699 ,,	5931 ,,
7	Butylamine	5532 ,,	5850 ,,
8	Aniline ..	5675 ,,	5900 ,,
9	O-Toluidine	5626 ,,	5928 ,,
10	M-Toluidine	5678 ,,	5941 ,,
11	P-Toluidine	5684 ,,	5950 ,,
12	O-Phenylene diamine	5694 ,,	5965 ,,
13	M-Phenylene ,,	5696 ,,	5968 ,,
14	P-Phenylene ,,	5699 ,,	5971 ,,
15	α-Napthylamine	5499 ,,	5597 ,,
16	β-Napthylamine	5222 ,,	5543 ,,
17	Pyridine	5692 ,,	5886 ,,
18	α-Picoline	5692 ,,	5907 ,,
19	Quinoline	5683 ,,	5851 ,,
20	Piperidine	5697 ,,	6022 ,,
21	Quinine ..	5537 ,,	5905 ,,
22	Cinchonidine	5557 ,,	5927 ,,
23	Nicotine	5695 ,,	5976 ,,
24	Morphine	5691 ,,	5962 ,,
25	Brucine ..	5697 ,,	5975 ,,

The fact that thiovioluric acid and all its salts show a marked blue fluorescence in solution shows that there exists some close relationship between the property of fluorescence and the chemical structure of these compounds. According to Hewitt (*Z. Physikal Chem.*, 1900, *34*, 1) fluorescence is conditioned by a process of oscillatory tautomerism or rapid vibration of the molecule between two structurally identical phases. To such a process he gave the name 'Double symmetrical tautomerism'. The two modifications emit and absorb alternately light rays of different vibrations and thus exhibit the phenomenon of fluorescence.

Examining the structure of iso-nitroso-thio-barbituric acid or thiovioluric acid in the light of the theory of Hewitt it can be seen that the oximino ketonic structure is capable of oscillation between the following nitroso enolic forms, both of which are structurally identical.

$$SC\underset{NH-C(OH)}{\overset{NH-CO}{<}}C-N=O \quad \rightleftharpoons \quad SC\underset{NH-CO}{\overset{NH-CO}{<}}C=N-OH \quad \rightleftharpoons \quad SC\underset{NH-CO}{\overset{NH-C(OH)}{<}}C-N=O$$

NITROSO ENOLIC FORM.   OXIMINO KETONIC FORM.   NITROSO ENOLIC FORM.

In both the forms it can form salts due to the mobile nature of the hydrogen atom. Such a configuration therefore is actually responsible for the property of fluorescence in these compounds. In fact it further verifies the existence of its nitroso enolic structure, assumed previously.

The alkaloidal salts of iso-nitroso-thio-barbituric acid all show optical rotation, although their rotation is always less than that of the parent alkaloid. It will be interesting to consider this fall in rotation, after salt formation, from the point of view of previous workers. Stewart (*J.*, 1907, *99*, 209) has shown that the greater the unsaturation of a substance, the greater will be its optical rotation and its absorption will also be greater. This was further confirmed by the work of Singh and Rai (*J. Indian Chem. Soc.*, 1926, *3*, 389) on coloured camphor compounds.

It is well known that the group —CH : N— present in many alkaloids is a negative unsaturated group and as soon as salt formation takes place, the two latent valencies of nitrogen become manifested, the structure becoming as follows :—

$$\overset{-CH}{\underset{N}{\|}} \quad \xrightarrow{HA} \quad \overset{-CH}{\underset{\underset{H\quad A}{N}}{\|}}$$
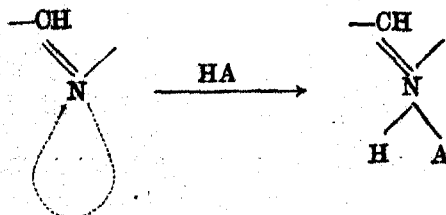
Hence if this unsaturation is removed after salt formation the resulting salt should have a less rotatory power than the original alkaloid. This has actually

been found true in the case of the salts of iso-nitroso-thio-barbituric acid and in one case (nicotine) the optical rotation has so much decreased that even optical inversion has taken place. The table 3 given at the end shows the lessening in the optical rotation. For the sake of comparison the optical rotation of the parent alkaloid is also given side by side. It may be noted, however, that the removal of strain from the molecule does not mean that the alkaloidal salts should be less coloured, since the actual colour of the salt is due to the other part of the molecule, viz. thiovioluric acid radical, which is itself sufficiently strained.

EXPERIMENTAL.

Iso-nitroso-thio-barbituric acid was prepared by passing a continuous stream of nitrous acid gas in a fresh ice cold suspension of thio-barbituric acid in water. The deep yellow pasty mass which resulted was quickly squeezed out and dried on a porous plate. When perfectly dry it can be recrystallized from absolute alcohol, dry acetone or a mixture of petroleum ether and acetone (1 : 5). The best results were obtained with the latter.

It crystallizes from alcohol in yellow lustrous needles, whereas from acetone in rectangular thin plates with saw-like edges. A microphotograph of the crystals from acetone is given below. When crystallized from a mixture
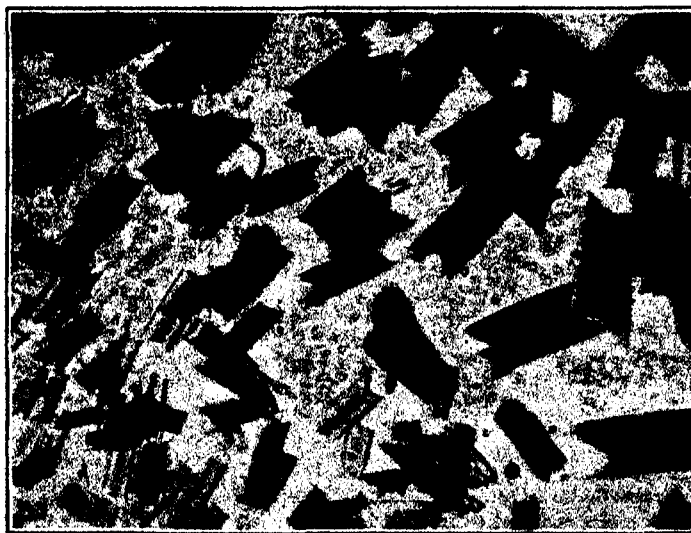
Microphotograph of the crystals of Iso-nitroso-thio-barbituric acid
(from dry acetone).

of petroleum ether and acetone it comes out as large well defined transparent hexagonal pyramids.

The solvent free substance has a bright lemon yellow colour and melts with decomposition at 210°C. It is sparingly soluble in cold water but gradually dissolves on warming. It readily dissolves in ethyl-alcohol, methyl-alcohol, acetone and ethyl acetate. It is rather sparingly soluble in ether and amyl alcohol and is almost completely insoluble in benzene, chloroform, carbon-tetrachloride, carbonbisulphide and petroleum ether.

It is a fairly strong acid having the dissociation constant $K = 10^{-5} \times 6.73$ and turns blue litmus red. With ferric chloride solution it gives a reddish colouration. It combines with both organic and inorganic bases, forming salts which are characteristically coloured and yield violet solutions. Most of the inorganic salts, like those of Ag, Fe, Cu, Pb, Ba, are all insoluble in water and come down as beautifully coloured precipitates when a drop of the acid solution is added to some soluble salt of these metals in water.

The salts of thiovioluric acid were all prepared by mixing equimolecular quantities of the acid and the base in alcoholic or aqueous solutions. On keeping, the salts separated out in fine needles, they were dried and recrystallized from 80% alcohol or water. The alkaloidal salts become sticky on exposure to moisture and hence they were best isolated by precipitation with ether and washed with the same solvent till perfectly dry.

The salts of iso-nitroso-thio-barbituric acid are all coloured in the solid state, the shades of which vary from light blue to deep violet, crimson and finally green. They yield fluorescent violet coloured solutions. They are quite stable when pure but gradually decompose when left under atmospheric conditions for a long time. They show no melting point but decompose when heated above 85°C. Nearly all of them are soluble in water or dilute alcohol to a lesser or greater extent. Their solutions show absorption bands between 4400Å — 6025Å. The alkaloidal salts are optically active too. A complete summary of the absorption maxima, dissociation constants and analytical results is given in tables 2, 3.

TABLE 2.

Salts of Iso-nitroso-thio-barbituric acid (Thiovioluric acid) with Alkalies, Aliphatic Amines and Aromatic Bases.

No.	Name of the Salt. ('T' stands for Thio-violurate).	Colour in solid state.	Colour in solution.	Absorption maxima in Angstrom units.	Molecular conductivity at N—128 in Mhos.	Dissociation constants.	Analytical results % sulphur. Theoretical value in brackets.
1	Thio-violuric acid	Brights yellow	Yellow	4403 Å	34·81 mhos.	$10^{-5} \times 6\cdot73$	18·39% (18·49)
2	Sodium T.	Carmine violet	Purple	5828 ,,	68·52 ,,	$10^{-3} \times 1\cdot532$	16·2% (16·41)
3	Potassium T.	Light blue	,,	5847 ,,	97·92 ,,	$10^{-3} \times 3\cdot345$	15·4% (15·17)
4	Lithium T.	Bright red	Violet	5825 ,,	71·12 ,,	$10^{-3} \times 3\cdot864$	15·04% (14·88)
5	Ammonium T.	Bluish violet	,,	5837 ,,	100·4 ,,	$10^{-3} \times 4\cdot05$	16·62% (16·85)
6	Methylamine T.	Light violet	,,	5829 ,,	79·68 ,,	$10^{-3} \times 3\cdot697$	15·63% (15·69)
7	Dimethylamine T.	Light blue	,,	5858 ,,	75·8 ,,	$10^{-3} \times 6\cdot567$	14·79% (14·68)
8	Trimethylamine T.	Chocolate brown	Purple	5820 ,,	53·02 ,,	$10^{-3} \times 8\cdot036$	13·51% (13·79)
9	Ethylamine T.	Light blue	,,	5870 ,,	69·53 ,,	$10^{-3} \times 2\cdot942$	14·89% (14·68)
10	Diethylamine T.	Deep blue	Bluish violet	5931 ,,	58·75 ,,	$10^{-3} \times 3\cdot245$	12·87% (13·01)
11	Isobutylamine T.	Light blue	,,	5850 ,,	58·68 ,,	$10^{-3} \times 2\cdot918$	12·78% (13·01)
12	Isoamylamine T.	,, ,,	,, ,,	5841 ,,	57·32 ,,	$10^{-3} \times 2\cdot635$	12·11% (12·30)
13	Aniline T.	Greyish blue	Reddish violet)	5900 ,,	...	...	12·34% (12·08)
14	O-Toluidine T.	Violet	,,	5928 ,,	...	...	11·55% (11·42)
15	M-Toluidine T.	Reddish fawn.	,,	5941 ,,	...	...	11·3% (11·42)
16	P-Toluidine T.	Greyish green	,,	5950 ,,	...	...	11·25% (11·42)
17	O-Anisidine T.	Violet Red	Bluish violet	5961 ,,	...	...	10·95% (10·81)
18	P-Phenetidine T.	Greyish blue	Reddish violet	5968 ,,	...	...	10·130% (10·32)
19	O-Phenylene diamine T.	Reddish brown	,,	5965 ,,	...	...	11·42% (11·39)
20	M-Phenylene diamine T.	Chocolate brown	,,	5968 ,,	...	...	11·2% (11·39)
21	P-Phenylene diamine T.	Grassy green	Purple violet	5971 ,,	...	...	11·29% (11·39)
22	M-Tolylene diamine T.	Deep chocolate	Reddish ,,	5976 ,,	...	...	11·14% (10·85)
23	α-Naphthylamine T.	Dark green	Violet blue	5597 ,,	...	...	10·27% (10·13)
24	β-Napthylamine T.	Light fawn	,,	5543 ,,	...	...	10·42% (10·13)
25	Pyridine T. (mono)	Greenish blue	Purple violet	5886 ,,	...	...	12·51% (12·70)
26	Pyridine T. (Complex)	Reddish brown	Reddish ,,	5879 ,,	...	...	15·42% (15·72)
27	Piperidine T.	Skyblue	Purple violet	6023 ,,	...	...	12·51% (12·60)
28	α-Picoline T. (Complex)	Violet grey	,, ,,	5907 ,,	...	...	14·95% (15·20)
29	Collidine T.	Fawn	Reddish ,,	5912 ,,	...	...	14·42% (14·25)
30	Quinoline T.	Violet grey	Purple	5861 ,,	...	...	13·81% (14·00)
31	Isoquinoline T.	Greyish brown	Reddish ,,	5864 ,,	...	...	13·87% (14·00)
32	Quinaldine T.	,, ,,	,, ,,	5869 ,,	...	...	13·31% (13·58)
33	Acridine T.	,, Brownish yellow	Yellowish ,,	6012 ,,	...	...	9·34% (9·1)

TABLE 3.

Alkaloidal salts of Iso-nitroso-thio-barbituric acid (Thiovioluric acid).

No.	Name of the Salt. ('T' stands for (Thiolurate).	Colour in solid state.	Colour in solution.	Absorption maxima in Angstrom units.	Rotation of alkaloid at 24°C.	Rotation of the salt at 24°C.	Analytical results % sulphur. Theoretical value in brackets.
34	Chinchonidine T.	Bluish green	Violet blue	3927 Å	−113·6°	−65°	6·71% (6·88)
35	Quinine T.	„ „	„ „	5905 „	−165·1°	−120°	6·459%(6·43)
36	Quinidine T.	Grassy green	Purple violet	5923 „	−250·2°	+112°	6·32% (6·43)
37	Nicotine T.	Brownish green	„ „	5976 „	−161·55°	+60°	9·82% (9·55)
38	Morphine T.	Greyish blue	Bluish violet	5968 „	−140·0°	−46·0°	6·81% (6·985)
39	Codeine T.	Dark green	Purple blue	5887 „	−132·0°	−54·0°	6·67% (6·78)
40	Brucine T. :						
	(a) Anhydrous	Greenish yellow	Violet	5975 „	−120·0°	−8·0°	5·40 % (5·64)
	(b) Hydrated	Bluish green	„	„ „	−120·0°	−8·0	5·40 % (5·64)

Fifth Ordinary General Meeting.

The Fifth Ordinary General Meeting of the National Institute of Sciences of India was held at 3 P.M. on Thursday the 25th March, 1937, in the Physics Lecture Theatre of the University of Allahabad.

The following Fellows were present :—

Prof. M. N. Saha, *President, in the Chair.*
Prof. B. Sahni, *Foreign Secretary.*
Prof. S. P. Agharkar, *Honorary Secretary.*
Prof. A. C. Banerji.
Prof. D. R. Bhattacharya.
Dr. S. Dutt.
Dr. H. R. Mehra.
Dr. C. W. B. Normand.
Dr. B. N. Prasad.
Dr. P. L. Srivastava.

In addition to the Fellows present there were about 27 visitors present.

The minutes of the Second Annual General Meeting were read and confirmed.

The Secretary reported that the following Ordinary Fellows had resigned their Fellowship :—

Dr. J. H. Hutton.
Dr. E. P. Metcalfe.

The Secretary reported the loss by death of the following Ordinary Fellow :—

Dewan Bahadur L. K. Ananthakrishna Iyer.

The following Ordinary Fellows were admitted as Fellows as per Rule 13 :—

Dr. B. N. Prasad.
Dr. P. L. Srivastava.

Prof. D. R. Bhattacharya and Dr. H. R. Mehra signed the duplicate obligation form as per Rule 13.

The following papers were read :—

1. On Propagation of Electromagnetic Waves through the Atmosphere. By M. N. Saha and R. N. Rai.
2. Radio Studies of the Upper Atmosphere at Allahabad. By G. R. Toshniwal, B. D. Pant and R. R. Bajpai. (Communicated by Prof. M. N. Saha.)
3. Chemical Examination of *Cleome pentaphylla* Linn. Part II. Constituents of the oil from the seeds. By R. N. Misra and S. Dutt.

4. Chemical Analysis of Indian Medicinal Plants. The active principle and other constituents of *Fumaria officinalis* Bedd. By R. R. Agarwal. (Communicated by Dr. S. Dutt.)

5. Chemical Examination of *Indigofera enneaphylla*, Linn. and the isolation of its active principle. By S. N. Chatterji and S. Dutt.

6. Dyes derived from Chrysoquinone. By M. P. Singh and S. Dutt.

7. Colour and Chemical Constitution of Iso-Nitroso Thio-Barbituric Acid and its Inorganic and Organic Salts. By R. Lal and S. Dutt.

8. The Infiltration of Golgi bodies and Mitochondria from the follicular epithelium to the egg. By D. R. Bhattacharya and M. D. L. Srivastava.

9. Prediction in Physiology. By W. Burridge.

10. Ranine Tuberculosis. By W. Burridge.

11. The Cardiac Valvular Reserve. By W. Burridge.

12. Colour Vision : Normal and Abnormal, for Physicists. By W. Burridge.

13. On differences in the Frog's ventricle. By W. Burridge.

14. Experiments with Sodium Iodoacetate. By P. C. Gupta. (Communicated by Prof. W. Burridge.)

The President was At Home to Fellows and visitors attending the meeting.

THE (0,0) BAND OF *OD*.

By M. Ishaq, *M.Sc., Ph.D., Department of Physics,*
Muslim University, Aligarh.

(Communicated by Prof. M. N. Saha.)

(*Read November 6, 1937.*)

INTRODUCTORY.

Observations of the spectra of diatomic hydride molecules have played an important part in the study of molecular spectra, since the small moments of inertia of these molecules lead to open-spaced band structures, which may be very fully resolved. Until recently, however, these spectra had contributed very little to the study of isotopic effects, for with a given pair of isotopes the hydrides yield the smallest displacements. The position has now been completely changed by the discovery of an isotope of hydrogen, viz. deuterium. The large ratio of the masses, 2 : 1 of the atoms of these isotopes yields displacements far greater than those obtained with any other pair of isotopes.

Johnston and Dawson (1933) photographed the *OD* bands obtained from a discharge in water containing 35% of heavy water. Johnston (1934) compared some results obtained from the unpublished data for some of the *OD* bands with Van Vleck's theory. Later on Shaw and Gibbs (1934) reported that they had photographed the *OD* (0,0) and (1,1) bands but their analysis has not, so far, appeared.

EXPERIMENTAL.

The discharge tube is shown in figure 1. The capillary was about 10 cms. in length and 3 mm. in diameter. The tube which was made of glass was immersed in a water tank to prevent it from being overheated. The bulb *C* containing heavy water was connected to a tube near the capillary.

The heavy water was obtained from the Imperial Chemical Industries Limited and was 99·2% pure.

The cylindrical electrodes were connected to a d.c. generator and the tube run at about 1200 volts and ¼ amp., the products of decomposition being continuously pumped out.

The band was photographed in the 4th order of a 10-foot concave grating at the Imperial College of Science, London, and the time of exposure was about three hours.

Measurements were made by comparison with the iron arc. Iron standards were taken from the *Transactions of the International Astronomical Union,*
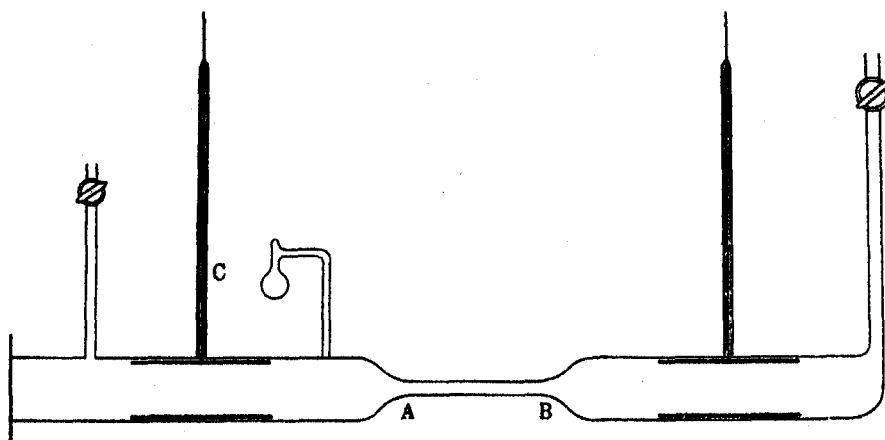
Fig. 1.   Discharge tube used in the production of the spectrum of *OD*.

4 (1932) supplemented from *Kayser Handbuch der Spectroskopie*, Vol. VII. The dispersion of the grating is about 1·3 A/mm.

THE STRUCTURE OF THE BAND.

The band shows two heads and is degraded towards the red. It resembles the *OH* band at λ 3064 analysed by Fortrat (1924) except for the contraction of the branches on account of the heaviness of deuterium as compared with hydrogen. This isotopic contraction is well marked in the case of $^{s}R_{21}$ branch which stands out alone and is not mixed with other branches as shown in fig. 2.
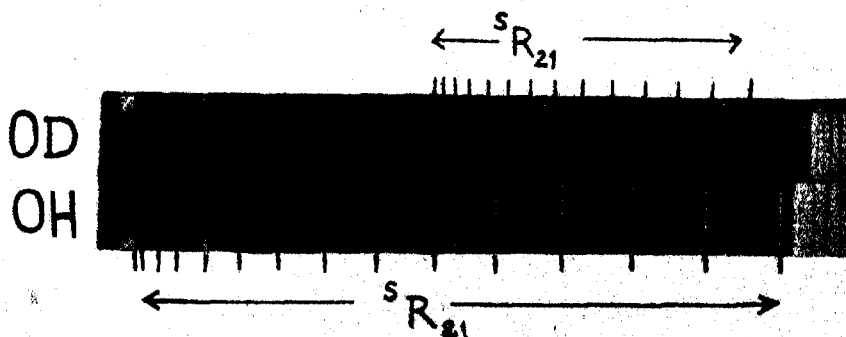
Fig. 2.   An enlargement from a plate taken in the 2nd order of a 10-foot concave grating showing the $^{s}R_{21}$ branches of the (0,0) bands of *OD* and *OH*.

The energy-level diagram shows the transition for the 12 branches, all of which have been recorded and are shown in fig. 3.
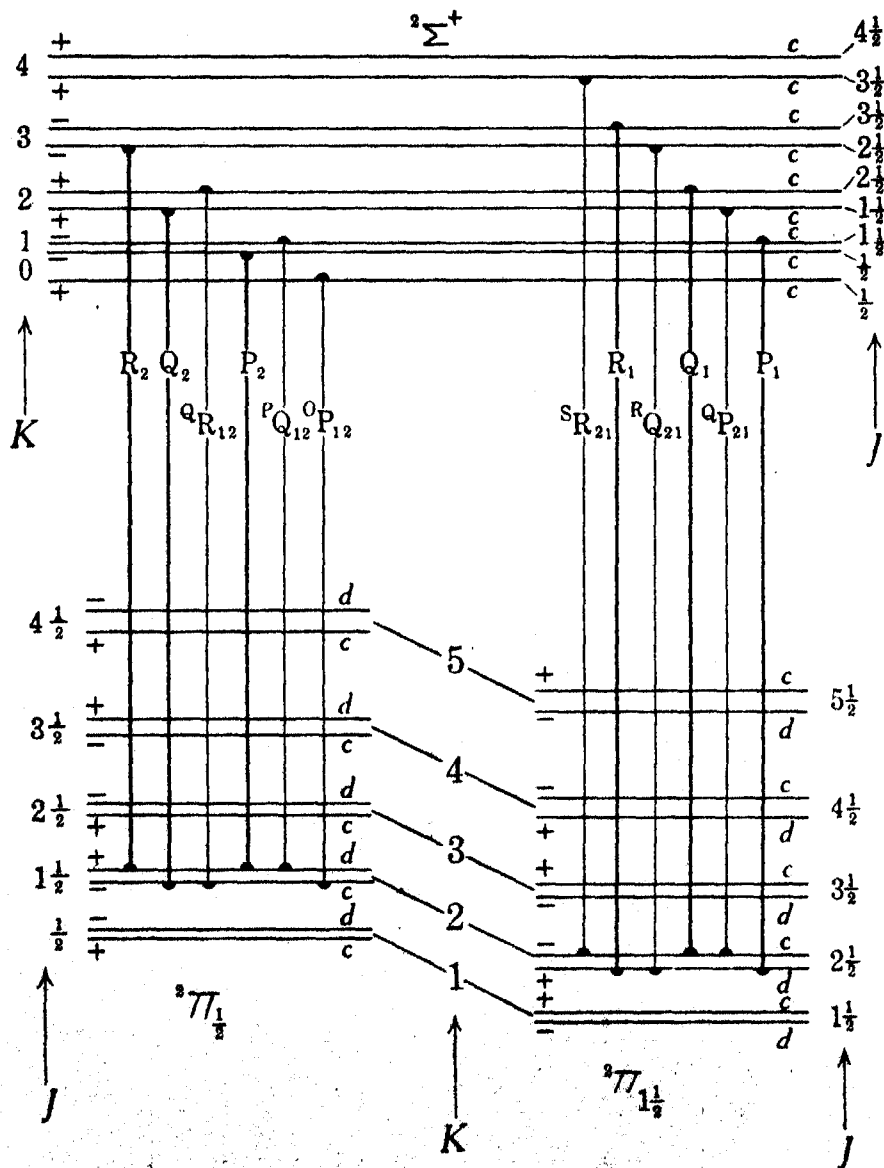
FIG. 3.   An energy-level diagram for a $^2\Sigma^+ \rightarrow {}^2\Pi_{inv.}$ transition showing the branches of the OD band at λ3065.

The OD bands, like those of OH, are attributed to the transition

$$^2\Sigma^+ + {}^2\Pi_{inv.}$$

The band with its branches is shown in fig. 4.

FIG. 4. An enlargement from a plate taken in the 4th order of a 10-foot concave grating showing the λ3065 band of *OD* and its branches.
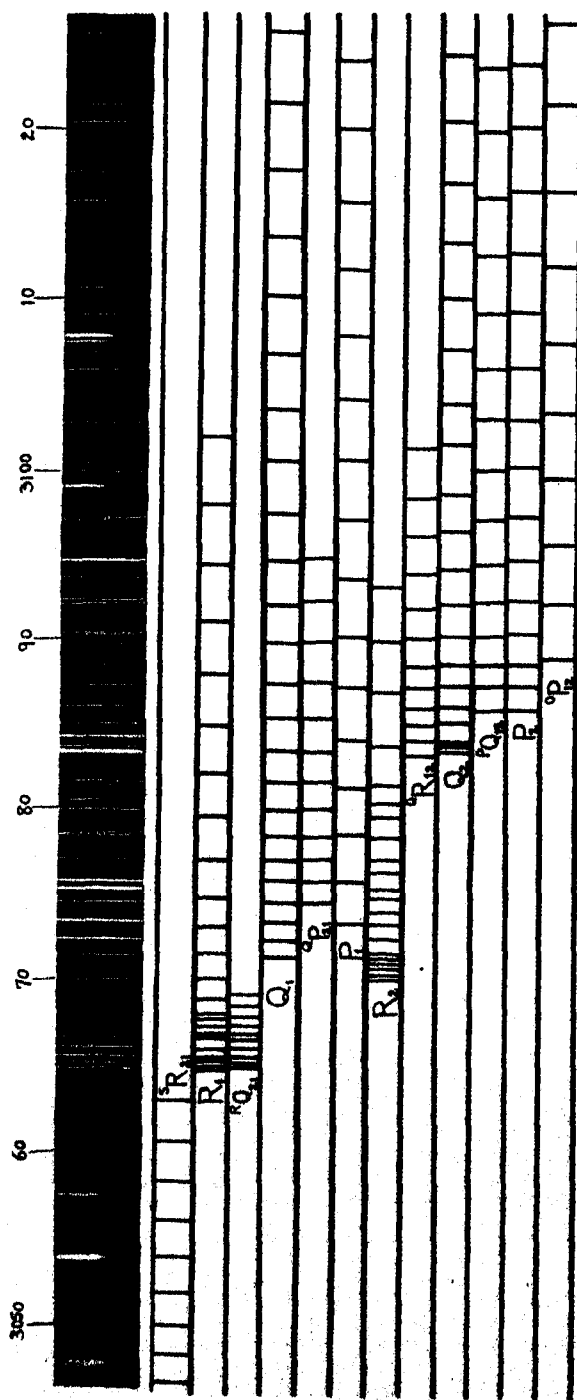
TRANSITIONS AND TERM VALUES.

The transitions are derived by the help of the selection rules

$$\Delta J = 0, \pm 1 \text{ and } + \rightleftarrows -$$

and are shown in the energy-level diagram.

T''_1 and T'_2 represent the rotational energy of the upper state.

T''_1 and T''_2 represent the rotational energy of the lower state.

The transitions are given below.

1. $R_1(K) \quad = T'_1(K+1) \quad -T''_{1d}(K)$
2. $Q_1(K) \quad = T'_1(K) \quad\quad -T''_{1c}(K)$
3. $P_1(K) \quad = T'_1(K-1) \quad -T''_{1d}(K)$
4. $^{S}R_{21}(K) \; = T'_2(K+2) \quad -T''_{1c}(K)$
5. $^{R}Q_{21}(K) = T'_2(K+1) \quad -T''_{1d}(K)$
6. $^{Q}P_{21}(K) = T'_2(K) \quad\quad -T''_{1c}(K)$
7. $R_2(K) \quad = T'_2(K+1) \quad -T''_{2d}(K)$
8. $Q_2(K) \quad = T'_2(K) \quad\quad -T''_{2c}(K)$
9. $P_2(K) \quad = T'_2(K-1) \quad -T''_{2d}(K)$
10. $^{O}P_{12}(K) = T'_1(K-2) \quad -T''_{2c}(K)$
11. $^{P}Q_{12}(K) = T'_1(K-1) \quad -T''_{1d}(K)$
12. $^{Q}R_{12}(K) = T'_1(K) \quad\quad -T''_{2c}(K)$

ROTATIONAL TERM DIFFERENCES FOR THE $^2\Sigma$ STATE.

The initial state has the characteristics of a $^2\Sigma$ state. It consists of a set of rotational levels each split up into two levels. The relative displacement of these levels is very small. This state falls under Hund's case b.

The rotational term differences

$$\Delta_2 F'(K) = F'(K+1) - F'(K-1)$$

are obtained from the following combinations

$$\Delta_2 F'(K) = R_1(K+1) - P_1(K+1)$$
$$= R_2(K+1) - P_2(K+1)$$

These are shown in table I.

The rotational constants for this state are calculated using the rotational energy function

$$F'(K) = B'_v K(K+1) + D'_v K^2(K+1)^2 + \ldots\ldots\ldots\ldots$$

whence

$$\Delta_2 F'(K) = (4K+2) [B'_v + 2D'_v(K^2 + K + 1) + \ldots\ldots\ldots\ldots\ldots]$$

The term differences are well represented by the above energy function with the values of B'_v and D'_v thus calculated. The values of the rotational constants are shown in table V.

TABLE I.

Rotational term differences for the $^2\Sigma$ State.

K	$R_1(K+1)-P_1(K+1)$	$R_2(K+1)-P_2(K+1)$
1	90·08 b	90·11
2	126·43	126·18 b
3	162·57	162·20 b
4	198·31 b	198·25 b
5	233·45 b	233·62
6	269·35	269·09
7	304·88	304·42
8	339·75	339·35
9	374·26	374·28
10	408·81	408·64
11	442·67 b	442·31 b
12	476·87	476·66
13	510·44	510·06
14	543·47	543·19
15	575·80	. . . .

b indicates that the difference is derived from blended lines.

ROTATIONAL TERM DIFFERENCES FOR THE $^2\Pi$ STATE.

The final state has the characteristics of a $^2\Pi$ state, the two heads corresponding to the two sub-states $^2\Pi_{1\frac{1}{2}}$ and $^2\Pi_{\frac{1}{2}}$ separated by 139·5 cm.$^{-1}$ Each sub-state has a set of rotational levels which are split up into two close component levels due to Λ-doubling. This state is intermediate between Hund's cases a and b.

The rotational term differences

$$\Delta_1 F''(K+\tfrac{1}{2}) = F''(K+1) - F''(K)$$

are evaluated from the following combinations:

$$\Delta_1 F''_{1cd}(K+\tfrac{1}{2}) = R_1(K) - Q_1(K+1) \left.\right\} {}^2\Pi_{1\frac{1}{2}}$$
$$\Delta_1 F_{1dc}(K+\tfrac{1}{2}) = Q_1(K) - P_1(K+1) \left.\right\}$$

$$\Delta_1 F''_{2cd}(K+\tfrac{1}{2}) = R_2(K) - Q_2(K+1) \left.\right\} {}^2\Pi_{\frac{1}{2}}$$
$$\Delta_1 F_{2dc}(K+\tfrac{1}{2}) = Q_2(K) - P_2(K+1). \left.\right\}$$

These are shown in table II.

TABLE II.

Rotational term differences for the $^2\Pi$ state.

K	$^2\Pi_{1\frac{1}{2}}$ state		$^2\Pi_{\frac{1}{2}}$ state	
	$R_1(K)-Q_1(K+1)$	$Q_1(K)-P_1(K+1)$	$R_2(K)-Q_2(K+1)$	$Q_2(K)-P_2(K+1)$
1	46·29	46·29 b	30·88 b	31·65
2	65·22	64·90	52·18	52·69 b
3	84·48 b	83·83	72·80	73·10 b
4	103·01	102·03 b	93·21	93·77
5	122·05 b	120·74 b	113·69 b	114·22
6	141·20	140·02	133·52	134·30
7	160·25	158·86	153·52	154·07
8	179·52	177·35	173·46 b	173·62
9	198·77 b	195·97	193·12 b	193·25 b
10	217·55	214·49 b	212·42 b	212·21 b
11	236·79	232·98	231·91	131·39
12	255·11 b	251·08	250·54 b	249·96
13	274·17	269·31	270·07	268·61
14	292·97	287·27	288·68	286·88
15	311·25	304·55	307·28	....
16	329·75	....	325·75	....
17	347·61 b	....	343·84	....
18	365·57	....	361·23 b	....
19	383·28	....	377·59	....
20	400·55	....	393·39	....
21	418·03	....	408·32	....
22	435·09	....	422·46	....
23	451·68	....	....	....

b indicates that the difference is derived from blended lines.

The difference between the values of $\Delta_1 F''_{dc}(K+\frac{1}{2})$ and $\Delta_1 F''_{cd}(K+\frac{1}{2})$ are a measure of the Λ-doubling, for

$$\Delta_1 F''_{dc}(K+\tfrac{1}{2}) - \Delta_1 F''_{cd}(K+\tfrac{1}{2}) = [F''_d(K+1) - F''_c(K+1)] + [F''_d(K) - F''_c(K)]$$
$$= \Delta \nu_{dc}(K+1) + \Delta \nu_{dc}(K)$$
$$= 2\delta_{dc}(K+\tfrac{1}{2}), \text{ say.}$$

The quantity $\delta_{dc}(K+\frac{1}{2})$ is thus the mean of the Λ-doubling in the levels $F(K+1)$ and $F(K)$. Its values are shown in table III.

TABLE III.

Λ—Doubling.

K	$^2\Pi_{1\frac{1}{2}}$ state	$^2\Pi_{\frac{1}{2}}$ state
1	0·00 b	+0·39 b
2	−0·16	+0·26 b
3	−0·33 b	+0·15 b
4	−0·49 b	+0·28
5	−0·65 b	+0·27 b
6	−0·59	+0·39
7	−0·70	+0·28
8	−1·08	+0·08 b
9	−1·40 b	+0·06 b
10	−1·53 b	−0·11 b
11	−1·90	−0·26 b
12	−2·01 b	−0·29 b
13	−2·43	−0·73
14	−2·82	−0·90
15	−3·35	. . . .

b indicates that the values are obtained from blended lines.

For the calculation of the rotational constants of the state the closed formula due to Hill and Van Vleck (1928) has been used.

$$F(J) = B\left[\left(J+\frac{1}{2}\right)^2 - \Lambda^2 \pm \left\{4\left(J+\frac{1}{2}\right)^2 + \frac{A}{B}\left(\frac{A}{B}-4\right)\Lambda^2\right\}^{\frac{1}{2}}\right] \ldots,$$

For a Π state $\Lambda = 1$

therefore

$$F(J) = B\left[\left(J+\frac{1}{2}\right)^2 - 1 \pm \left\{4\left(J+\frac{1}{2}\right)^2 + \frac{A}{B}\left(\frac{A}{B}-4\right)\right\}^{\frac{1}{2}}\right] \ldots,$$

Now splitting the formula into its two parts we get

$$F_1(J) = B\left[\left(J+\frac{1}{2}\right)^2 - 1 + \frac{1}{2}\left\{4\left(J+\frac{1}{2}\right)^2 + \frac{A}{B}\left(\frac{A}{B}-4\right)\right\}^{\frac{1}{2}}\right] \ldots,$$

$$F_2(J) = B\left[\left(J+\frac{1}{2}\right)^2 - 1 - \frac{1}{2}\left\{4\left(J+\frac{1}{2}\right)^2 + \frac{A}{B}\left(\frac{A}{B}-4\right)\right\}^{\frac{1}{2}}\right] \ldots;$$

Summing these parts and adding a term containing the second rotational constant D,

$$F_1(J) + F_2(J) = 2B[(J+\tfrac{1}{2})^2 - 1] + 2D[(J+\tfrac{1}{2})^2 - 1]^2 + \ldots,$$

and taking the first differences,

$$\Delta_1 F_1(J) + \Delta_1 F_2(J) = 4(J+1)[B + D(2J^2 + 4J + \tfrac{1}{2}) \ldots].$$

The rotational constants shown in table V have been obtained by the help of this equation.

For the calculation of A, take the difference of the above expressions

$$F_1(J) - F_2(J) = B\left\{4\left(J+\frac{1}{2}\right)^2 + \frac{A}{B}\left(\frac{A}{B}-4\right)\right\}^{\frac{1}{2}}\ldots,$$

therefore

$$\left(\frac{A}{B}-2\right)^2 = \left\{F_1(J) - F_2(J)\right\}^2 \bigg/ B^2 - 4\left\{\left(J+\frac{1}{2}\right)^2 - 1\right\}.$$

The intervals

$$F_1(J) - F_2(J) = R_1(J) - Q_2(J)$$
$$= Q_1(J) - P_2(J)$$

if the small effects of A-doubling in the $^2\Pi$ state and spin-doubling in the $^2\Sigma$ state are neglected. The values of A for each value of J thus calculated are shown in table IV.

TABLE IV.

Values of A.

J	Cm. [1]
$1\frac{1}{2}$	$-139\cdot13$
$2\frac{1}{2}$	$-138\cdot49$
$3\frac{1}{2}$	$-139\cdot68$
$4\frac{1}{2}$	$-139\cdot50$
$5\frac{1}{2}$	$-139\cdot90$
$6\frac{1}{2}$	$-139\cdot90$
$7\frac{1}{2}$	$-139\cdot65$
$8\frac{1}{2}$	$-139\cdot56$
$9\frac{1}{2}$	$-139\cdot41$
Mean	$-139\cdot47$

TABLE V.

Band	B'_v	D'_v	B''_v	D''_v
OD $\lambda3065$ (0,0)	$9\cdot020$	$-0\cdot580 \times 10^{-3}$	$9\cdot870$	$-0\cdot400 \times 10^{-3}$
OH $\lambda3064$ (0,0)	$16\cdot955$	$-2\cdot00 \times 10^{-3}$	$18\cdot516$	$-1\cdot82 \times 10^{-3}$

Values for OH are taken from Tanaka and Koana (1933).

SUMMARY.

The $\lambda3065$ band of OD has been photographed in the 4th order of a 10-foot concave grating.

The band like that of OH is the (0,0) band of a $^2\Sigma^+ \to {}^2\Pi_{inv.}$ transition.

An analysis of the rotational structure has been made and the values of the rotational constants determined.

The values of the rotational constants have been compared with those of the corresponding OH band.

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K	R_1			Q_1			P_1	
	i	ν Vac.		i	ν Vac.		i	ν Vac.
1	4	32582·67		3	32547·00		4	32528·49
2	4	590·79		8b	536·38		2b	500·71
3	3	597·91		6b	525·57		5	471·48
4	4	32604·31		4b	513·43		5	441·74
5	4b	609·71		5	501·30		5	411·40
6	4	614·01		6	487·66		5b	380·56
7	4	617·02		5	472·81		6	347·64
8	6	618·83		5	456·77		6	313·95
9	3	619·17		5	439·31		2	279·42
10	4	617·60		6b	420·40		4	243·34
11	3	614·72		4	400·05		4	205·91
12	4b	609·71		3	377·93		4	167·07
13	4	603·72		6	354·60		5	126·85
14	4	32595·73		4	329·55		3	085·29
15	4	585·75		3	302·82		4	042·28
16	3	574·07		5	274·50		3	31998·27
17	2b	560·09		4	244·32			
18	3	544·37		3	212·48			
19	2	526·60		3	178·80			
20	5	506·51		3	143·32			
21	2	484·87		3	106·02			
22	4	460·79		3	066·84			
23	4	434·50		3	025·70			
24	4	406·08		3	31982·82			
25	3	375·31						
26	5	342·29						
27	3	306·83						
28	4	269·12						
29	3	228·96						
30	1	186·10						
31	1	140·86						

K	R_2 i	R_2 ν Vac.	Q_2 i	Q_2 ν Vac.	P_2 i	P_2 ν Vac.
1	2	32451·28	5	32415·62	3	32397·36
2	3	474·08	6b	420·40	6	383·97
3	4	493·89	4	421·90	7b	367·71
4	4	511·00	4	421·09	7b	348·80
5	6b	525·57	5	417·79	4	327·32
6	4	537·19	5	411·88	3	303·57
7	6	546·67	5	403·67	4	277·58
8	4	554·02	5	393·15	4	249·60
9	3	558·88	5b	380·56	4	219·53
10	3	561·59	5b	365·76	4	187·31
11	3	562·09	7b	349·17	4	153·55
12	2b	560·09	4	330·18	4	117·78
13	3	556·88	6	309·55	3	080·22
14	3	551·00	4	286·81	3	040·95
15	3	543·12	5	262·32	3	31999·93
16	3	533·10	3	235·84		
17	4	520·84	4	207·35		
18	8b	505·85	5	177·00		
19	2	488·03	4	144·62		
20	2	467·63	3	110·44		
21	1	444·38	4	074·24		
22	3	418·35	3	036·06		
23	0	389·19	3	31995·89		
24	1	357·05				
25	0	322·36				

SATELLITES.

K	$^S R_{21}$ i	$^S R_{21}$ ν Vac.	$^R Q_{21}$ i	$^R Q_{21}$ ν Vac.	$^Q P_{21}$ i	$^Q P_{21}$ ν Vac.
1	3	32636·77		....		....
2	4	662·48	4	32590·35		....
3	3	667·49	4	597·42		....
4	3b	32711·51		....	4b	32513·43
5	3b	734·58	4	609·03	2b	500·71
6	3	756·21	4b	613·21	4	487·00
7	3	776·63	3	616·20	2	472·00
8	2	795·37		....	2	455·76
9	2	32812·58		....	2	438·18
10	1	828·20		....		....
11	1	842·05	4b	613·21	1	398·66
12	0	854·09		....	2	376·69
13	0	863·54		....	1	353·16
14	0	871·76	1	593·99	4	327·85
15	0	877·42	0	583·83	0	301·16
16			1	571·88		

SATELLITES.

K	$^QR_{12}$		$^PQ_{12}$		$^OP_{12}$	
	i	ν Vac.	i	ν Vac.	i	ν Vac.
1		. . . .	0	32397·83		. . . .
2		. . . .		. . . .	5b	32365·76
3	4	32422·42		. . . .	3	331·91
4		. . . .	1b	350·31	3	295·26
5		. . . .		. . . .	4	256·08
6	2	412·59	1	304·41	2	214·51
7	2	404·52	2	278.41	2	170·69
8	1	394·08	2	250·42	2	124·87
9	2	381·58	3	220·38	3d	077·13
10	0	366·96	2	188·56	2	027·48
11	1b	350·31	2	154·67	1	31976·21
12		. . . .	2	118·97		
13	0	311·17	1	081·86		
14	1	288·47	2	042.62		
15	0	264·03	1	001·61		
16	0	237·89				

CATALOGUE OF WAVE NUMBERS.*

All lines which have been measured are included in the Catalogue.

ν Vac.	i	$^{S}R_{21}$	R_1	$^{R}Q_{21}$
32877·42	0	15	..	..
871·76	0	14	..	..
863·54	0	13	..	..
854·09	0	12	..	..
842·05	1	11	..	..
828·20	1	10	..	..
812·58	1	9	..	..
795·37	2	8	..	..
776·63	2	7	..	..
756·21	3	6	..	..
734·58	3	5	..	..
711·51	3	4	..	..
687·49	3	3	..	..
662·48	4	2	..	..
636·77	3	1	..	..
619·17	3	..	0	..
618·83	6	..	8	..
617·60	4	..	10	..
617·02	4	..	7	..
616·20	3	..	..	7
614·72	3	..	11	..
614·01	4	..	6	..
613·21	4	..	..	6, 11
610·21	4	..	..	..
609·71	4	..	5, 12	..
609·03	4	..	..	5
604·31	4	..	4	..
603·72	4	..	13	..
603·30	1	..	..	..
597·91	4	..	3	..
597·42	4	..	..	3
595·73	4	..	14	..
593·99	1	..	..	14
592·91	1	..	..	..
590·79	4	..	2	..

* This method of designation of each branch at the top of the column and K values opposite the appropriate wave-numbers was first adopted by me in *Proc. Roy. Soc.* A, **159**, 110, (1937).

ν Vac.	i	R_1	$^R Q_{21}$	Q_1	P_1	R_2
32590·35	4	..	2	..	..	..
587·89	1	..	..	..	..	..
585·75	4	15	..	..	..	..
583·83	0	..	15	..	..	..
582·96	2	..	..	..	..	..
582·67	4	1	..	..	..	..
577·41	1	..	..	..	..	..
574·07	3	16	..	..	..	..
571·88	1	..	16	..	..	..
569·84	1	..	..	..	..	..
568·72	1	..	..	..	..	..
566·33	1	..	..	..	..	..
564·75	1	..	..	..	..	..
562·09	3	..	..	..	..	11
561·59	2	..	..	..	..	10
560·61	2	..	..	..	..	..
560·09	2	17	..	..	..	12
558·88	3	..	..	..	..	9
557·28	1	..	..	..	..	..
556·88	3	..	..	..	..	13
554·40	1	..	..	..	..	..
554·02	4	..	..	..	..	8
551·00	3	..	..	..	..	14
548·05	1	..	..	..	..	..
547·00	3	..	..	1	..	..
546·67	6	..	..	..	..	7
544·37	3	18	..	..	..	..
543·12	3	..	..	..	..	15
539·33	1	..	..	..	..	..
537·19	4	..	..	..	..	6
536·38	8b	..	..	2	..	..
533·10	3	..	..	..	..	16
531·09	1	..	..	..	..	..
528·69	1	..	..	..	..	..
528·49	4	..	..	..	1	..
526·60	2	19	..	..	..	..
525·98	1	..	..	..	..	..
525·57	6b	..	..	3	..	5
525·04	4b	..	..	..	..	..
520·84	4	..	..	..	..	17

ν Vac.	i	R_1	Q_1	$Q_{P_{21}}$	P_1	R_2
32516·19	1	..	..	..	..	..
514·32	3	..	..	..	..	..
513·94	5	..	..	..	..	..
513·43	4	..	4	4	..	..
512·27	1	..	..	..	..	..
511·42	1	..	..	..	..	..
511·00	4	..	..	..	..	4
506·51	5	20	..	..	..	..
505·85	8b	..	..	..	..	18
501·78	2	..	..	..	..	..
501·30	5	..	5	..	..	..
500·71	2	..	..	5	2	..
500·32	3	..	..	..	..	..
498·55	2	..	..	..	..	..
494·13	1	..	..	..	..	..
493·89	4	..	..	..	..	3
493·20	1	..	..	..	..	..
490·41	1	..	..	..	..	..
489·96	3	..	..	..	..	..
488·03	2	..	..	..	..	19
487·66	6	..	6	..	..	..
487·00	4	..	..	6	..	..
484·87	2	21	..	..	..	..
483·69	1	..	..	..	..	..
482·21	1	..	..	..	..	..
476·91	1	..	..	..	..	..
474·39	1	..	..	..	..	..
474·08	3	..	..	..	..	2
473·23	1	..	..	..	..	..
472·81	5	..	7	..	..	..
472·00	2	..	..	7	..	..
471·48	5	..	..	..	3	..
470·71	1	..	..	..	..	..
467·63	2	..	..	..	..	20
463·58	1	..	..	..	..	..
460·79	4	22	..	..	..	..
458·17	1	..	..	..	..	..
457·11	3	..	..	..	..	..
456·77	5	..	8	..	..	..
455·76	2	..	..	8	..	..

ν Vac.	i	R_1	Q_1	$Q_{P_{21}}$	P_1	R_2	$Q_{R_{12}}$	Q_2	$P_{Q_{12}}$	P_2
32452·58	1	..	..	..	..	..	..	..	..	..
451·28	2	..	..	..	..	1	..	..	..	..
450·51	3	..	..	..	..	..	..	..	..	..
444·38	1	..	..	..	..	21	..	..	..	..
443·29	1	..	..	..	..	..	..	..	..	..
442·21	3	..	..	..	..	..	..	..	..	..
441·74	5	..	..	..	4	..	..	..	..	..
439·71	2	..	..	..	..	..	..	..	..	..
439·31	5	..	9	..	..	..	..	..	..	..
438·18	2	..	..	9	..	..	..	..	..	..
436·48	1	..	..	..	..	..	..	..	..	..
434·50	4	23	..	..	..	..	..	..	..	..
431·89	1	..	..	..	..	..	..	..	..	..
431·09	1	..	..	..	..	..	..	..	..	..
428·45	1	..	..	..	..	..	..	..	..	..
427·25	3	..	..	..	..	..	..	..	..	..
422·42	4	..	..	..	..	..	3	..	..	..
421·90	4	..	..	..	..	..	..	3	..	..
421·09	4	..	..	..	..	..	..	4	..	..
420·40	6	..	10	..	..	..	..	2	..	..
418·35	3	..	..	..	..	22	..	..	..	..
417·79	5	..	..	..	..	..	..	5	..	..
417·12	1	..	..	..	..	..	..	..	..	..
415·62	5	..	..	..	..	..	..	1	..	..
412·59	2	..	..	..	..	..	6	..	..	..
412·38	2	..	..	..	..	..	..	..	..	..
411·88	5	..	..	..	..	..	..	6	..	..
411·40	5	..	..	..	5	..	..	..	..	..
406·08	4	24	..	..	..	..	..	..	..	..
404·52	2	..	..	..	..	..	7	..	..	..
403·67	5	..	..	..	..	..	..	7	..	..
401·88	3	..	..	..	..	..	..	..	..	..
400·48	2	..	..	..	..	..	..	..	..	..
400·05	4	..	11	..	..	..	..	..	..	..
398·66	1	..	..	11	..	..	..	..	..	..
397·83	0	..	..	..	..	..	..	..	1	..
397·36	3	..	..	..	..	..	..	..	..	1
394·08	1	..	..	..	..	..	8	..	..	..
393·50	1	..	..	..	..	..	..	..	..	..
393·15	5	..	..	..	..	..	..	8	..	..

ν Vac.	i	R_1	Q_1	$Q_{P_{21}}$	P_1	R_2	$Q_{R_{12}}$	Q_2	$P_{Q_{12}}$	P_2	$O_{P_{12}}$
32391·34	1	..	..	..	..	..	..	..	..	..	..
390·79	1	..	..	..	..	..	..	..	..	..	..
389·19	0	..	..	..	..	23	..	..	..	..	..
383·97	6	..	..	..	..	..	..	..	..	2	..
381·58	2	..	..	..	..	..	9	..	..	..	..
380·56	5	..	..	..	6	..	..	9	..	..	..
380·01	5	..	..	..	..	..	..	..	..	..	..
378·57	1	..	..	..	..	..	..	..	..	..	..
377·93	4	..	12	..	..	..	..	..	..	..	..
376·69	2	..	..	12	..	..	..	..	..	..	..
375·31	3	25	..	..	..	..	..	..	..	..	..
374·14	3	..	..	..	..	..	..	..	..	..	..
367·71	7b	..	..	..	..	..	..	..	..	3	..
366·96	0	..	..	..	..	..	10	..	..	..	..
366·13	2	..	..	..	..	..	..	..	..	..	..
365·76	5	..	..	..	..	..	..	10	..	..	2
359·71	1	..	..	..	..	..	..	..	..	..	..
358·31	1	..	..	..	..	..	..	..	..	..	..
357·05	1	..	..	..	..	24	..	..	..	..	..
355·02	1	..	..	..	..	..	..	..	..	..	..
354·60	6	..	13	..	..	..	..	..	..	..	..
353·16	1	..	..	13	..	..	..	..	..	..	..
350·31	1	..	..	..	..	..	11	..	4	..	..
349·17	7b	..	..	..	..	..	..	11	..	..	..
348·80	7b	..	..	..	..	..	..	..	..	4	..
347·64	6	..	..	..	7	..	..	..	..	..	..
344·05	5	..	..	..	..	..	..	..	..	..	..
342·29	5	26	..	..	..	..	..	..	..	..	..
331·91	3	..	..	..	..	..	..	..	..	..	3
330·46	1	..	..	..	..	..	..	..	..	..	..
330·18	4	..	..	..	..	..	..	12	..	..	..
329·55	4	..	14	..	..	..	..	..	..	..	..
327·85	4	..	..	14	..	..	..	..	..	..	..
327·32	4	..	..	..	..	..	..	..	..	5	..
324·79	1	..	..	..	..	..	..	..	..	..	..
322·36	0	..	..	..	..	25	..	..	..	..	..
320·58	1	..	..	..	..	..	..	..	..	..	..
314·37	2	..	..	..	..	..	..	..	..	..	..
313·95	6	..	..	..	8	..	..	..	..	..	..
311·62	4	..	..	..	..	..	..	..	..	..	..

ν Vac.	i	R_1	Q_1	$^Q P_{21}$	P_1	R_2	$^Q R_{12}$	Q_2	$^P Q_{12}$	P_2	$^O P_{12}$
32311·17	0	..	..	..	..	..	13	..	..	..	..
309·84	2	..	..	..	..	..	..	..	..	..	..
309·55	6	..	..	..	..	..	..	13	..	..	..
306·83	3	27	..	..	..	..	..	..	..	..	..
304·41	1	..	..	..	..	..	..	..	6	..	..
304·17	3	..	..	..	..	..	..	..	..	..	..
303·57	3	..	..	..	..	..	..	..	..	6	..
302·82	3	..	15	..	..	..	..	..	..	..	..
301·16	0	..	..	15	..	..	..	..	..	..	..
295·28	3	..	..	..	..	..	..	..	..	..	4
289·77	1	..	..	..	..	..	..	..	..	..	..
288·47	1	..	..	..	..	..	14	..	..	..	..
287·25	2	..	..	..	..	..	..	..	..	..	..
286·81	4	..	..	..	..	..	..	14	..	..	..
286·30	1	..	..	..	..	..	..	..	..	..	..
281·41	1	..	..	..	..	..	..	..	..	..	..
279·42	2	..	..	..	9	..	..	..	..	..	..
279·17	4	..	..	..	..	..	..	..	..	..	..
278·41	2	..	..	..	..	..	..	..	7	..	..
277·58	4	..	..	..	..	..	..	..	..	7	..
276·82	2	..	..	..	..	..	..	..	..	..	..
274·87	1	..	..	..	..	..	..	..	..	..	..
274·50	5	..	16	..	..	..	..	..	..	..	..
269·12	4	28	..	..	..	..	..	..	..	..	..
264·03	0	..	..	..	..	..	15	..	..	..	..
262·32	5	..	..	..	..	..	..	15	..	..	..
256·08	4	..	..	..	..	..	..	..	..	..	5
253·94	1	..	..	..	..	..	..	..	..	..	..
250·42	2	..	..	..	..	..	..	..	8	..	..
249·60	4	..	..	..	..	..	..	..	..	8	..
244·32	4	..	17	..	..	..	..	..	..	..	..
243·63	1	..	..	..	..	..	..	..	..	..	..
243·34	4	..	..	..	10	..	..	..	..	..	..
239·54	2	..	..	..	..	..	..	..	..	..	..
237·89	0	..	..	..	..	..	16	..	..	..	..
236·23	1	..	..	..	..	..	..	..	..	..	..
235·84	3	..	..	..	..	..	..	16	..	..	..
230·26	2	..	..	..	..	..	..	..	..	..	..
228·96	3	29	..	..	..	..	..	..	..	..	..
220·38	3	..	..	..	..	..	..	..	9	..	..

ν Vac.	i	R_1	Q_1	P_1	Q_2	$^P Q_{12}$	P_2	$^O P_{12}$
32219·53	4	..	..	..	..	..	9	..
218·12	1	..	..	..	..	..	..	..
216·50	1	..	..	..	..	..	..	..
214·51	3	..	..	..	..	..	..	6
212·48	3	..	18	..	..	..	..	..
207·72	1	..	..	..	..	..	..	..
207·35	4	..	..	..	17	..	..	..
205·91	4	..	..	11	..	..	..	..
199·72	2	..	..	..	..	..	..	..
198·21	1	..	..	..	..	..	..	..
196·87	1	..	..	..	..	..	..	..
195·03	1	..	..	..	..	..	..	..
192·41	3	..	..	..	..	..	..	..
191·27	2	..	..	..	..	..	..	..
190·52	2	..	..	..	..	..	..	..
189·54	2	..	..	..	..	..	..	..
188·56	2	..	..	..	..	10	..	..
187·31	4	..	..	..	..	..	10	..
186·10	1	30	..	..	..	..	..	..
183·65	1	..	..	..	..	..	..	..
183·03	1	..	..	..	..	..	..	..
182·38	1	..	..	..	..	..	..	..
179·16	1	..	..	..	..	..	..	..
178·80	3	..	19	..	..	..	..	..
177·62	1	..	..	..	..	..	..	..
177·00	5	..	..	..	18	..	..	..
170·69	2	..	..	..	..	..	..	7
169·05	2	..	..	..	..	..	..	..
168·84	1	..	..	..	..	..	..	..
167·07	4	..	..	12	..	..	..	..
164·24	1	..	..	..	..	..	..	..
158·89	2	..	..	..	..	..	..	..
155·44	2	..	..	..	..	..	..	..
154·67	2	..	..	..	..	11	..	..
153·93	1	..	..	..	..	..	..	..
153·55	5	..	..	..	..	..	..	..
146·96	2	..	..	..	..	..	..	..
145·07	1	..	..	..	..	..	..	..
144·62	4	..	..	..	19	..	..	..
143·74	1	..	..	..	..	..	..	..

ν Vac.	i	R_1	Q_1	P_1	Q_2	$^P Q_{12}$	P_2	$^O P_{12}$
32143·32	3	..	20	..	..	..	..	..
140·86	1	31	..	..	..	..	..	..
134·05	1	..	..	..	..	..	..	..
132·80	1	..	..	..	..	..	..	..
131·43	1	..	..	..	..	..	..	..
130·15	1	..	..	..	..	..	..	..
129·15	1	..	..	..	..	..	..	..
127·25	1	..	..	..	..	..	..	..
126·85	5	..	..	13	..	..	..	..
124·87	2	..	..	..	..	..	..	8
121·33	1	..	..	..	..	..	..	..
120·92	1	..	..	..	..	..	..	..
118·97	2	..	..	..	..	12	..	..
117·78	4	..	..	..	..	..	12	..
116·77	2	..	..	..	..	..	..	..
113·52	1	..	..	..	..	..	..	..
112·62	2	..	..	..	..	..	..	..
111·74	1	..	..	..	..	..	..	..
110·85	1	..	..	..	..	..	..	..
110·44	3	..	..	..	20	..	..	..
107·97	2	..	..	..	..	..	..	..
106·45	1	..	..	..	..	..	..	..
106·02	3	..	21	..	..	..	..	..
103·55	1	..	..	..	..	..	..	..
102·10	2	..	..	..	..	..	..	..
098·52	2	..	..	..	..	..	..	..
095·98	2	..	..	..	..	..	..	..
095·09	1	..	..	..	..	..	..	..
092·28	2	..	..	..	..	..	..	..
091·31	2	..	..	..	..	..	..	..
088·77	2	..	..	..	..	..	..	..
085·29	3	..	..	14	..	..	..	..
084·16	2	..	..	..	..	..	..	..
082·89	2	..	..	..	..	..	..	..
081·86	1	..	..	..	..	13	..	..
080·22	3	..	..	..	..	..	13	..
078·29	2	..	..	..	..	..	..	..
077·13	3d	..	..	..	..	..	..	9
075·98	1	..	..	..	..	..	..	..
074·62	2	..	..	..	..	..	..	..

ν Vac.	i	Q_1	P_1	Q_2	$^PQ_{12}$	P_2	$^OP_{12}$
32074·24	4	..	..	21	..	..	..
072·85	2	..	..	..	..	..	..
070·77	1	..	..	..	..	..	..
068·68	3	..	..	..	..	..	..
067·94	1	..	..	..	..	..	..
067·24	1	..	..	..	..	..	..
066·84	3	22	..	..	..	..	..
064·94	1	..	..	..	..	..	..
060·04	2	..	..	..	..	..	..
055·75	3	..	..	..	..	..	..
054·08	1	..	..	..	..	..	..
053·24	4	..	..	..	..	..	..
052·42	1	..	..	..	..	..	..
051·08	1	..	..	..	..	..	..
042·61	2	..	..	..	14	..	..
042·28	4	..	15	..	..	..	..
041·24	1	..	..	..	..	..	..
040·95	3	..	..	..	..	14	..
036·38	3	..	..	..	..	..	..
036·06	3	..	..	22	..	..	..
035·47	1	..	..	..	..	..	..
031·62	1	..	..	..	..	..	..
031·12	1	..	..	..	..	..	..
027·48	2	..	..	..	..	..	10
026·51	2	..	..	..	..	..	..
025·70	4	23	..	..	..	..	..
019·85	2	..	..	..	..	..	..
018·11	3	..	..	..	..	..	..
014·61	2	..	..	..	..	..	..
010·58	1	..	..	..	..	..	..
004·03	1	..	..	..	..	..	..
003·49	2	..	..	..	..	..	..
002·67	1	..	..	..	..	..	..
002·26	3	..	..	..	..	..	..
001·61	1	..	..	..	15	..	..
31999·93	3	..	..	..	..	15	..
998·27	3	..	16	..	..	..	..
997·74	3	..	..	..	..	..	..
996·33	3	..	..	..	..	..	..
995·89	3	..	..	23	..	..	..
993·49	1	..	..	..	..	..	..
991·88	3	..	..	..	..	..	..
988·98	1	..	..	..	..	..	..
983·77	1	..	..	..	..	..	..
982·82	3	24	..	..	..	..	..
980·42	1	..	..	..	..	..	..
976·88	3	..	..	..	..	..	..
976·21	1	..	..	..	..	..	11
974·86	1	..	..	..	..	..	..

Sixth Ordinary General Meeting.

The Sixth Ordinary General Meeting of the National Institute of Sciences of India was held in the Auditorium of the All-India Institute of Hygiene and Public Health, Calcutta, from 11 A.M. to 4-30 P.M. on the 27th and from 10 A.M. to 4-30 P.M. on the 28th August, 1937, with an adjournment for lunch from 1 P.M. to 2-30 P.M. on both the days.

The following Fellows were present :—

Prof. M. N. Saha, *President, in the Chair* (on the 27th only).
Brevet-Col. R. N. Chopra, *Vice-President.*
Sir U. N. Brahmachari, *Additional Vice-President.*
Rai Bahadur Dr. S. L. Hora, *Honorary Treasurer.*
Dr. B. Prashad, *Editor of Publications.*

Mr. C. C. Calder (on 27th only).	Dr. R. B. Lal.
Dr. H. Chaudhuri ,,	Dr. S. C. Law (on 27th only).
Dr. B. N. Chopra.	Prof. J. N. Mukherjee (on 27th only).
Dr. A. L. Coulson (on 27th only).	Prof. P. Neogi.
Prof. S. Datta ,,	Prof. N. R. Sen (on 27th only).
Prof. J. Ghosh ,,	Rao Bahadur T. S. Tirumurti (on 28th only).
Dr. B. S. Guha ,,	Dr. A. C. Ukil (on 27th only).
Dr. K. V. Krishnan	Mr. D. N. Wadia ,,
Dr. M. S. Krishnan (on 27th only).	Mr. W. D. West ,.

Prof. S. P. Agharkar
Dr. A. M. Heron (on 27th } *Honorary Secretaries.*
only).

In the absence of the President, Brevet-Col. R. N. Chopra, Vice-President, took the Chair on the 28th August.

Besides the Fellows there were about 60 and 45 visitors present on the 27th and 28th August respectively.

The following Fellows had intimated their inability to attend :—

Prof. R. P. Paranjpye, Dr. F. G. Percival, Lt.-Col. H. E. Shortt and Sir Gerald Trevor.

The following Ordinary Fellows were admitted as Fellows as per Rule 13 :—

Prof. J. Ghosh.   Dr. R. B. Lal.   Dr. A. C. Ukil.
Dr. M. S. Krishnan.   Dr. S. C. Law.

The Secretary reported that the Osmania University, Hyderabad (Deccan) had sanctioned a grant of Rs.300 per annum for two years to the National Institute and that the Government of India has sanctioned a grant-in-aid of Rs.6,000 per annum from 1937-38 financial year.

The following papers forming part of a Symposium on the malaria problem in India were read and discussed :—

1. Therapeutics of antimalarial drugs. By R. N. Chopra.
2. Urban malaria in the United Provinces. By A. C. Banerji.

3. Methods of forecasting malaria epidemics. By R. B. Lal.

4. Malaria in Portuguese India. By Froilano de Mello.

5. Physical factors in mosquito ecology. By R. Senior White.

6. Irrigation and malaria. By W. C. Sweet.

7. Flood and flush schemes in Bengal. By T. A. Curry.

8. Surface and subsoil drainage. By F. C. Griffin.

9. Irrigation and malaria in Madras Presidency. By S. G. Masillamani.

10. Topography of land in relation to malaria. By M. O. T. Iyengar.

11. *Anopheles ludlowii* survey in and around Calcutta. By P. Sen.

12. Malaria and its relation to agriculture in India. By G. C. Chatterjee.

13. Antimalarial operations in Delhi. By M. K. Afridi.

14. Control of anopheline breeding in irrigation channels by Paris green. By B. A. Rao.

15. Drug prophylaxis in malaria by the use of quinine and plasmoquine in the field. By J. D. Sinha.

16. Spleen and resistance to malaria and hæmoglobinuria. By K. V. Krishnan.

17. Mosquito control in Calcutta. By K. L. Chowdhury.

18. Larvivorous Fish. By G. C. Chatterjee.

19. Larvicidal Fish. By S. L. Hora.

20. Experimental studies on ape malaria with reference to its use in therapy for nervous conditions. By R. N. Chopra, B. M. Das-Gupta and B. Sen.

21. Pharmacology of plasmochin with special reference to its action in pregnancy. By B. B. Dikshit.

22. Biochemical changes in the blood of monkeys developing malarial hæmoglobinuria and their significance in the aetiology and treatment of blackwater fever in man. By K. V. Krishnan and N. G. Pai.

23. Transmission of *P. inui* to man. By B. M. Das-Gupta.

24. Natural parasites of mosquitoes in India. By M. O. T. Iyengar.

25. Observations on the nutrition of *Panchax panchax*. By S. L. Hora and K. K. Nair.

26. Observations on the bionomics of *Panchax panchax*. By A. G. Fraser.

27. The development of bird malaria parasites in endothelial cells. By H. N. Ray.

28. Salt water *rossi* as a malaria carrier. By D. N. Roy.

29. The pathology of malarial spleen. By M. N. De.

An account of the Symposium will be published in the *Proceedings* in due course.

Seventh Ordinary General Meeting.

The Seventh Ordinary General Meeting of the National Institute of Sciences of India was held at 2-30 P.M. on Saturday, the 6th November, 1937 in the Physics Lecture Theatre of the University of Delhi.

The following Fellows were present :—

Prof. M. N. Saha, *President* (in the chair).
Prof. S. S. Bhatnagar, *Vice-President*.
Sir Bryce Burt
Prof. J. C. Ghosh.
Khan Bahadur M, Afzal Husain.
Dr. S. Krishna.
Dr. D. S. Kothari.
Prof. J. N. Ray.
Rao Bahadur B. Viswanath.
Prof. S. P. Agharkar, *Honorary Secretary*.

Besides the Fellows there were about 50 visitors present.

The minutes of the last Ordinary General Meeting, held on the 27th and 28th August, 1937, at Calcutta, were read and confirmed.

The Secretary announced that since the last Ordinary General Meeting, news had been received of the death of the following Honorary Fellows :—

Prof. Albert Heim on the 31st August, 1937.
Lord Rutherford of Nelson on the 20th October, 1937.

On the motion of the President the following resolutions were passed by the meeting, all present standing :—

(i) The National Institute of Sciences of India places on record its deep sense of sorrow and loss to Science owing to the death of Prof. Albert Heim, one of the Honorary Fellows of the Institute, which took place at Zurich on the 31st August, 1937.

(ii) The National Institute of Sciences of India place on record its deep sense of sorrow and loss to Science owing to the death of the great physicis Lord Rutherford of Nelson, one of the Honorary Fellows of the Nationa Institute, which took place on the 20th October, 1937.

The Secretary announced that the following had been elected Ordinary Fellows of the National Institute :—

Prof. Y. Bharadwaja.
Principal B. L. Bhatia.
Prof. G. R. Paranjpe.
Dr. H. Srinivasa Rao.
Dr. K. Rangadharma Rao.

Prof. M. R. Siddiqi.
Prof. A. C. Sircar.
Dr. M. B. Soparkar.
Hon'ble Sir Shah M. Sulaiman.
Col. F. C. Temple.

Sir Shah Sulaiman who was present as a visitor was admitted as an Ordinary Fellow under Rule 13 and signed the obligation.

The Secretary announced that the following had been elected Honorary Fellows of the Institute :—

Prof. Ludwig Diels.   Prof. Robert Robinson.
Sir James G. Frazer.   Dr. C. M. Wenyon.

The proposed change in Rule 7(*b*) was considered, in view of the opinions expressed by Fellows. It was resolved to agree to the change being made, with the addition of the words ' not more than ' before the ' number of vacancies ', etc.

The Secretary was authorized to refer the alteration to the votes of Resident Fellows as per provisions of Rule 78.

The following papers were read :—

(1) The 0-0-Band of OD. By M. Ishaq. (Communicated by Prof. M. N. Saha).

(2) The Theory of Liquids. By T. S. Wheeler.

(3) A study of the behaviour of some common varieties of sugar-cane in reference to the attack of borers. By H. S. Pruthi and E. S. Narayanan.

(4) Joule-Thomson effect and adiabatic changes in degenerate gas. By D. S. Kothari.

(5) The chemical fixation of nitrogen at low temperature and its significance in agriculture. By B. Ramamurty. (Communicated by Rao Bahadur B. Viswanath.)

(6) The propagation of electromagnetic waves through the Atmosphere. By M. N. Saha and K. B. Mathur.

(7) Joule-Thomson expansion of a non-degenerate gas. By B. N. Srivastava. (Communicated by Prof. M. N. Saha.)

Mr. Larola of the Delhi University thanked the National Institute for having met at Delhi and chosen the University as the meeting place. He expressed the view that the National Institute should meet more often in different seats of learning and encourage local workers. The President thanked the Delhi University for permitting the meeting being held in their premises.

With a vote of thanks to the chair the meeting terminated.

After the meeting Sir Shah Sulaiman entertained Fellows to tea at his residence, 8 Albuquerque Road, New Delhi.

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